

Metal cation exchanged cellulose as new layer material for identification and separation of organic dyes

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ABSTRACT

Cellulose, an organic material has been used in the form of thin layer after treating with aqueous salt solutions of metal cations to utilize its chromatographic performance for identification of organic dyes with preliminary separation by thin layer chromatographic technique. The newly developed metal cation exchanged cellulose in combination of surfactants-mediated mobile phase systems has proved novel stationary phase for achieving important separations of organic dyes by thin layer chromatography. Several important separations of organic dyes achieved using proposed thin layer chromatographic systems have been listed. It is the first report on the use of metal cation exchanged cellulose as stationary phase in combination of surfactants-mediated mobile phase systems for identification and selective separation of organic dyes including food dyes.

Keywords: Metal cation treated cellulose, Separation, Identification, Thin layer chromatography, Surfactant

INTRODUCTION

The problem of identification and analysis of dyes have become exceedingly complex because a large number dyestuff is marketed under much larger number of names. Therefore, the appropriate analytical tool is needed for the analysis of the dyes. Among, the methods available for the routine analysis of synthetic dyes. Thin layer chromatography (TLC) is the most useful technique due to (I) low cost (II) wide choice of mobile phases (III) flexibility in sample detection (IV) high sample through put (V) easy handling. Thin layer chromatography has reported its wide range of applicability in separation and identification of synthetic dyes[1-6]. The most of the TLC methods reported for the analysis of dyes involved the use mixed organic solvent systems, while the little work has been reported on the use of micellar mobile phase [7-9]. The most favoured stationary phase was the silica gel [10-12] as compared to the less preferred phases of alumina [13], cellulose [14] and mixed solvent phase [15-18]. Cellulose is an organic material with similar functions as expected from silica gel. It is composed of D-glucopyranose units couple β -glycosidically at position 1 and 4 by oxygen atoms. It is used anion exchanger for separation of metals. The TLC methods reported so far did not used cellulose impregnated with aqueous salt solution of metal cations as stationary phase. The present study involved the use of cellulose impregnated with different metal cations the stationary phase and aqueous solution of surfactants SDC, CTAB and Triton X-100 belonging to the different classes as mobile phases. These aqueous surfactants solutions were also used in combination with the acetone as eluents.

MATERIALS AND METHODS

All experiments were performed at 30 ± 2 °C.

APPARATUS

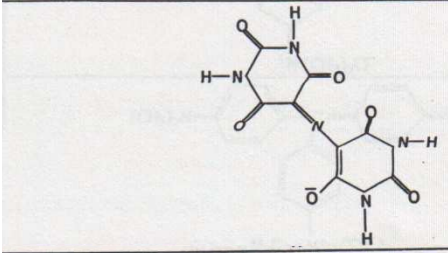
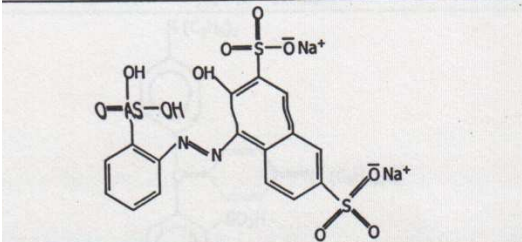
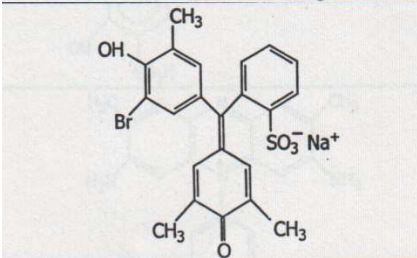
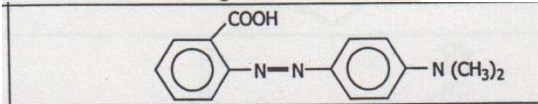
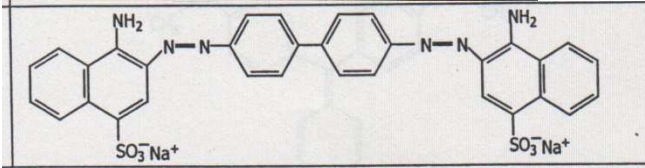
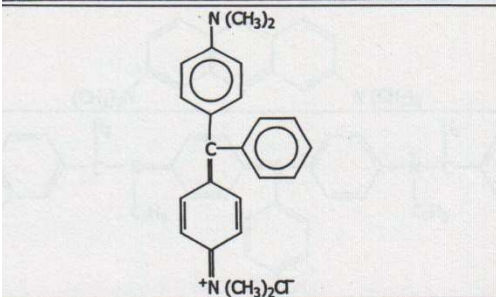
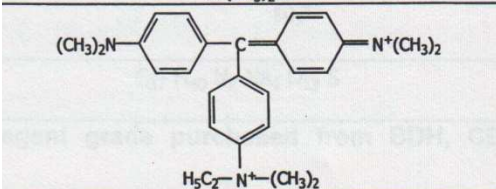
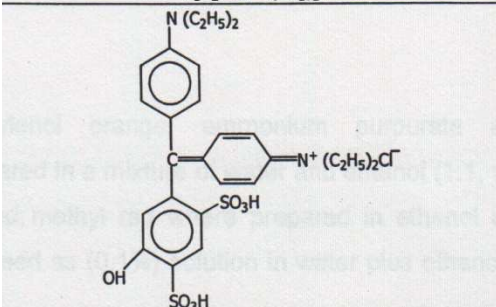
A TLC applicator, 20×3.5 cm glass plates and 24×6 cm glass jar were used.

REAGENTS

Cellulose, Barium Chloride, strontium chloride (Merck, Mumbai, India); sodium dodecyl sulphate, (SDS) (BDH, India); N-cetyl-N, N-trimethyl ammonium bromide (CTAB), Triton X-100 and acetone (CDH, India) were used. All reagents were of analytical reagent grade. The names, structure of dyes and their code numbers are summarised in table 1.

Table 1: Names, Codes and Structures of dyes used in the studies

Dyes	Code	Structure
Bromocresol green	1	
Xylenon orange	2	
Aluminone	3	
Alizarin Red S	4	
1-(2-Pyridylazo)-2-Naphthol (PAN)	5	
Pyrocatechol violet	6	
Bromopyrogallol red	7	

Ammonium Purpurate	8	
Thorin Indicator	9	
Bromocresol Purple	10	
Methyl red	11	
Congo red	12	
Malcohit green	13	
Brilliant green	14	
Patent blue V	15	

Saffranine	16	
Crystal violet	17	
Metanil yellow	18	
Methylene blue	19	
Light green	20	
Methylthymol blue sodium salt	21	$C_{37} H_{40} N_2 Na_4 O_{13} S$

All the dyes were of Analytical Reagent grade purchased from BDH, CDH, Qualigens and Merck India.

TEST SOLUTIONS

Test solutions (0.2%) of xylene orange, ammonium purpurate and methylthymol blue sodium salt were prepared in a mixture of water and ethanol (1:1, v/v) whereas solutions of (0.1%) of PAN and methyl red were prepared in ethanol and water respectively. All other dyes were used as (0.1%) solution in water plus ethanol in 1:1 ratio by volume.

DETECTION

All the dyes were visually detected according to their original colour. The composition with code of various stationary and mobile phase are summarised in table 2 and table 3.

Table 2: Code and composition of various stationary phases

CODE	COMPOSITION
S ₁	Cellulose impregnated with 10 % aqueous BaCl ₂
S ₂	Cellulose impregnated with 10 % aqueous srCl ₂
S ₃	Cellulose impregnated with 5 % aqueous BaCl ₂
S ₄	Cellulose impregnated with 5 % aqueous srCl ₂

Table 3 : Code and composition of various mobile phases

CODE	COMPOSITION
M ₁	SDS (0.081 M)
M ₂	SDS (0.00081 M)
M ₃	CTAB (0.009 M)
M ₄	CTAB (0.00009 M)
M ₅	Triton X-100 (0.001 M)
M ₆	Triton X-100 (0.00001 M)
M ₇	SDS (0.081 M) + Acetone (6:4)
M ₈	CTAB (0.009 M) + Acetone (6:4)
M ₉	Triton X-100 (0.001 M) + Acetone (6:4)
M ₁₀	Triton X-100 (0.00001 M) + Acetone (6:4)

PROCEDURE

About 10µl of test solution was spotted on TLC plates with the help of micropipette. The plates were developed in the chosen solvent system by the ascending technique. The solvent ascent was fixed 10 cm in all cases. After development was completed the plate was withdrawn from glass jar and dried at room temperature. TLC plates were then exposed to light. The dyes were detected as coloured spots. The R_L (R_F of leading front) and R_T (R_F of trailing front) values for each spot were determined and the R_F values and hRF were calculated:

$$R_F = (R_L + R_T) / 2$$

$$hRF = (100 \times R_F)$$

SEPARATION

For separation of dyes equal volumes of dyes to be resolved were mixed and 5µl of resultant mixture was loaded on TLC plate. The plate was developed with mobile phase. The spots were detected and R_F values of separated dyes were determined.

SEPARATION FOR DESIRED SAMPLES

For the desired separation (depending on their R_F values) equal volumes of samples were mixed and 0.01 ml of resultant mixture was loaded on activated TLC plates. The TLC plates were developed with selected mobile phase, the spots were detected and R_F values of the separated component were determined. The separation has been summarised in table.

PREPARATION OF TLC PLATES

The plates were prepared by mixing cellulose with aqueous solution of metal cations in 1:3 ratios with constant shaking until homogeneous slurry is obtained. The slurry was then coated onto glass plates with the help of a TLC applicator to give a layer of 0.25mm thickness. The plates were air dried at room temperature (27 °C) and then activated by heating for 1h at 100 °C in an electrically heated oven. The activated plates were stored in closed chamber until used.

RESULTS AND DISCUSSION

The chromatography of the 21 different dyes was performed on cellulose impregnated with different metal cation using various solvent systems. The results of the present study are summarized in table 4-6. First of all the different concentration of metal cation (Ba and Sr) belonging to the same group as an impregnating material was group as an impregnating material was used with .081 % aqueous SDS (M₁) as mobile phase. The result of different concentration (5-10%) of Ba and Sr as an impregnating material on cellulose present in table 4. In 10 % aqueous BaCl₂ as impregnate as cellulose. The dyes (3, 6, 8 and 12) are not detected on the plates. The dyes (14, 18 and 20) show low hRF values as compared to the other dyes which show higher h R_F value. In case on 10 % aqueous SrCl₂ as impregnate on cellulose, the dyes (6, 3 and 12) are not detected while the low hRF values are observed for the dyes (3, 4, 5, 9, 17, 18, 19 and 20) and higher hRF value are observed for (7 and 21) as compared to other dyes. It is clear from the result that the higher mobility of dyes was obtained and cellulose impregnated with 10 % aqueous BaCl₂ (S₁) as compared to the 10 % aqueous SrCl₂ (S₂) as impregnating material on cellulose layers. This may be due to the layer size of Ba²⁺ as compared to Sr²⁺. This confers to that these dyes show low affinity towards Ba²⁺ as compared to Sr²⁺ ion. The affect of concentration of this metal cation as an impregnating material was also studied in order to find out the optimum concentration of impregnated for the chromatography of these dyes. In 5 % aqueous BaCl₂ impregnated on cellulose (S₃), dyes (8 and 12) are not detected. While the dyes(3,4 and 7) show low hRF values and the higher hRF values are observed for the dyes (1,2,6,9,10,15,20 and 21) as compared to the other studied dyes. In case of 5% aqueous SrCl₂ impregnated on cellulose (S₄),dyes (3, 8 and 12) are not detected on the

plate. While the dyes (15 and 20) show low hRF value is compared to other dyes (1, 2, 5, 6,7, 8, 9, 10, 11 and 21) which show hRF values. It is clear from the results that in the lower concentration of those metal cations as impregnating material on cellulose the higher hRF values of dyes are obtained as compound the 10 % aqueous impregnated layers. The significant motilities of these dyes were obtained on 5% aqueous BaCl₂ impregnated layer as compared to 5% aqueous SrCl₂ cellulose layer.

In order to find a useful solvent system for the chromatography for these dyes the two different concentrations of three surfactants belonging to different classes were used for the chromatography for these dyes. These surfactants were also used in combination with acetone as solvent systems. The results of the solvent systems (M₁-M₁₀) used with 5% aqueous BaCl₂ impregnated on cellulose (S3) for the chromatography of dyes are presented in table 2. In M₁ (0.081 M SDS) the dyes (8 and 12) are not detected while the dyes (1, 2, 6, 9, 10, 15, 20 and 21) show higher hRF value as compared to other dyes. In the solvent system M₂ (0.0081 M SDS) the dyes (8 and 12) are not detected while the dyes (1, 2, 10, and 21) show higher hRF values as compared to their other dyes. The dyes (3, 6, 8 and 12) are not detected in the solvent systems M₃ (0.009 M CTAB) while few dyes (16 and 11) show low hRF value as compared to other dyes. In the solvent system M₄ (0.00009 M CTAB) the dyes (6, 8 and 12) are not detected while the dyes (4, 5, 11, 15, 18, 19 and 20) show low hRF value as compared to other dyes. In case of the solvent system M₅ (0.001 M Triton X-100) the dyes (3, 6 and 8) are not detected in plates, while the dyes (1, 2, 10, 15, 18 and 21) show higher hRF value as compared to other dyes. In case of solvent system M₆ (0.00001 M triton X-100) almost some pattern was observed with only slight difference in hRF values as compared to the solvent system M₅ (0.001 M triton X-100). The dyes (6 and 8) are not detected in the solvent system M₇ (0.081 M SDS + acetone (6:4)) while other dyes show higher hRF values as compared to the dyes (4) which show low mobility. The some pattern was observed in the solvent system M₈ (0.001 M CTAB + acetone 6:4) as obtained in the solvent system M₇ with only difference that few dyes show slight higher hRF values. Almost the same pattern in the mobility trend was observed in the solvent systems M₉ (0.001 M Triton X-100 + acetone 6:4) and M₁₀ (0.00001 M Triton X-100 + acetone 6:4) where the dyes (3, 6 and 8) are not detected and the only few dyes (4, 7 and 9) show low hRF value as compared to the other dyes.

From the separation point of view our investigation was not restricted to the particular solvent system or on a particular stationary phase. In this way we have separated several dyes from their binary mixtures. The results of the separation of their dyes are presented in table 3.

Table 4: hRF= (100 × R_F) values of dyes on various stationary phases (S₁-S₄) using 0.081 % aqueous SDS (M₁) as mobile phase

Dyes	hR _F			
	S1	S2	S3	S4
1	55.5 (b)	31.5 (b)	56 T (G)	73.5 (b)
2	41 T (br)	38 (T)(Y)	66 (Y)	61.5 T (Y)
3	ND	18 (O)	13 (br)	ND
4	6.5 (br)	6 (R)	6.5 (R)	6 (R)
5	36.5 T (O)	19.5 (Y)	46.5 T (Y)	67 (br)
6	ND	ND	68 (br)	68 (Y)
7	39.5 T (V)	54 T (Pr)	27 T (Pr)	73.5 (Pr)
8	ND	ND	ND	ND
9	44.5 (R)	19 T (O)	57.5 T (O)	71 (O)
10	71 T (B)	42.5 T (Y)	68 (Y)	76 (Y)
11	43 (P)	32 (P)	38.5 (P)	60 T (P)
12	ND	ND	ND	ND
13	32 T (b)	24.5 T (G)	38.5 T (G)	33.5 T (G)
14	27.5 T (G)	32 T (G)	37 T (G)	40.5 T (G)
15	30.5 (G)	28 T (G)	52 (G)	0.69 (G)
16	30.5 T (P)	29.5 T (P)	33.5 T (P)	38.5 T (P)
17	33 T (V)	20.5 T (Pr)	37.5 T (V)	42.5 T (V)
18	10 (Y)	12 (Y)	31.5 T (Y)	48.5 T (Y)
19	35 T (b)	17 T (B)	38.5 T (b)	41.5 T (b)
20	27.5 T (Pr)	3.5 (Pr)	62.5 (Pr)	19.5 T(Pr)
21	52 (Y)	60 (Y)	64.5 (Y)	78 (Y)

b=Blue, G=Green, P=Pink, br=Brown,,o =orange, Y=yellow, V= Violet, Pr=purple, t= Toiling, R= Red, B=Black, N.D.=Not Detected

Table 5: hRF values of dyes on cellulose layers impregnated with using various mobile phases 5% aqueous BaCl₂ (S₃) (M₁- M₁₀)

Dyes	hRF									
	M ₁	M ₂	M ₃	M ₄	M ₅	M ₆	M ₇	M ₈	M ₉	M ₁₀
1	56 (T)	41	42.5(T)	42(T)	86.5	81 (T)	7.5	87	94.5	91.5
2	66	42.5(T)	41(T)	47(T)	92	85	71.5	0.06,89	94.5	94
3	13	6.5	ND	7.5	ND	ND	32.5(T)	ND	ND	ND
4	6.5	0.6	39.5(T)	6.5	32(T)	31 (T)	32(T)	21.5(T)	35(T)	26.5(T)
5	46.5 (T)	3.5	57.5(T)	4	62(T)	88	70.5	79.5	95	93.5
6	68	9.5	ND	ND	ND	ND	ND	95.5	ND	ND
7	27 (T)	31 (T)	39.5(T)	41 (T)	38.5(T)	42.57(T)	49(T)	31(T)	28.5(T)	18(T)
8	ND	ND	ND	ND	ND	ND	ND	ND	ND	ND
9	57.5 (T)	27.5(T)	43(T)	20.5(T)	25.5(T)	25.5(T)	30.5(T)	20.5(T)	24(T)	24(T)
10	68	64	41(T)	0.52(T)	92.5	76	86.5	91.5	94.5	93
11	38.5	14.5	59.5	13	38.5(T)	55(T)	76.5	81.5	90.5	80
12	ND	ND	ND	ND	22.5(T)	21(T)	4	7	8.5	8
13	38.5(T)	26.5(T)	39.5(T)	24.5(T)	48 (T)	50(T)	81	76.5(T)	94.5	94.5
14	37 (T)	12.5	63	14.5	77(T)	86	66(T)	83.5	95	82.5
15	52	6.5	75.5	3	92	82	70(T)	89.5	94	88.5
16	33.5(T)	12.5	9.5	11.5	43 (T)	39(T)	42.5(T)	47(T)	80(T)	70(T)
17	37.5(T)	12,13.5	25(T)	13	49(T)	49(T)	44.5(T)	50(T)	50(T)	50(T)
18	31.5(T)	6	36.5(T)	9	87	91	72	79.5(T)	95	90
19	38.5(T)	13.5	13	13	12	11.5	37.5(T)	47.5	38(T)	54
20	62.5	2.5	34.5(T)	4.5	40	45(T)	69.5	96.5	94	95
21	64.5	63	55 (T)	52	92.5	87.5	87.5	90	98	94.5

T= Tailed Spot N.D. = Not detected

Table 6. Separation achieved experimentally on cellulose impregnating with metal cations using various solvent systems

Mobile phase	hRF Values		
	Stationary phase	Combination of dyes	separation
M ₁	S ₃	3+6	3 (18.5), 6
		3+10	3 (75), 10 (71)
		11+4	11 (72), 4 (8.5)
		3+21	3(10), 21 (76.5)
M ₂	S ₃	1+3	1 (59.5), 3(4)
		1+5	1 (66.5), 5 (5)
		10+5	10 (82), 5 (5)
		21+14	21 (86.5), 14 (12)
		10+11	10 (83), 11 (17)
		10+18	10 (77), 18(10)
M ₃	S ₃	21+19	21 (75.5), 19 (12.5)
		19+14	19 (10.5), 14 (87.5)
M ₄	S ₃	16+11	16 (14.5), 11 (89.0)
		11+21	11 (38), 21 (79)
M ₅	S ₃	18+21	18 (13), 21 (75)
		1+19	19 (15), 1 (21)
M ₆	S ₃	10+19	19 (9.5), 10 (17)
		18+19	19 (11.5), 18 (11)
M ₇	S ₃	2+19	2 (90.5), 19 (5.5)
		5+12	12 (5.5), 5 (74)
		10+12	12 (5.5), 10 (95)
		13+12	12 (9), 13 (89)
M ₈	S ₃	21+12	12 (6), 21 (92)
		6+12	12 (13.5), 6(90)
		14+12	12 (14), 14 (92)
M ₉	S ₃	15+12	12 (14.5), 15 (95)
		5+12	12 (12.5), 5 (95)
M ₁	S ₄	10+4	4 (10), 10 (72.5)
M ₁	S ₁	4+15	4 (6.5), 15 (71.5)

CONCLUSION

In present studies we achieved some very good separation of dyes from their binary mixtures. It is clear from the result that the higher mobility of dyes was obtained on cellulose impregnated with 10 % aqueous BaCl₂ (S₁) as compared to the 10 % aqueous SrCl₂ (S₂) impregnated material on cellulose layers. This is the confirmation of these dyes show low affinity towards Ba²⁺ as compared to Sr²⁺ ion.

The above study also confirm that the metal cation exchanged cellulose in combination of surfactants-mediated mobile phase is a novel stationary phase for achieving important separations of organic dyes by thin layer chromatography

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