Effect of Electrolyte Concentration on Dyeing Process of Cotton

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Abstract: Two reactive dyes and six electrolytes were used in dyeing cotton in order to observe the electrolyte effect on dye shades. The quality and amount of the electrolytes used were found to influence the depth of dye shade due to dye-fiber interaction, Suitable amount of proper electrolyte facilitates rapid migration of dye from the solution to the fiber resulting in deeper shades. It was observed that potassium sulphate in the range of 7-8% produced best results. Sodium sulphate was comparable whereas ammonium salts gave poor results.

Keywords: Cotton dyeing, electrolytes, dye-fibre interaction, potassium sulphate, reactive dyes

Introduction

The molecule of a reactive dye contains one or more reactive groups capable of forming a covalent bond with a compatible fibre group. The main steps in the dyeing procedure with a dye of this type comprise adsorption on the fibre, diffusion into the fibre and reaction with the hydroxyl groups of cellulose or amino groups of wool (Peters, 1975; Hildebrand, 1972).

The quality of dyeing (depth and fastness) is directly related to the quantity of dye chemically fixed to the fibre. During the dyeing process, the fabrics are generally in an alkaline environment (Bohnert, 1959) and electrolytes tend to reduce the charge on the fibre (Chavan *et al.,* 1983) thus facilitating the transfer of dye from solution into the fibre due to common ion effect (Noah *et al.,* 1986). Electrolyte screens the forces of repulsion between the negatively charged cellulose and the dyestuff anions. The salt also exercises a positive effect on the rate of reaction of the dye itself, since generally speaking polar media will facilitate the formation of the transition state. The dependence of the rate of reaction on the ion concentration of the reactive medium is known as primary salt effect (Froast and Pearson, 1961).

Reaction between the reactive dyes and the cellulose fibres is equally dependent on the pH of the dye bath. In this case the dissociation of the hydroxyl groups in the cellulose, whether cotton or viscose, is essential for those dyes that require alkaline conditions for the dye to react with the fibre (Dawson, 1981). Dissociation is achieved by having a dye bath solution of pH 8-12, which is obtained by adding sodium bicarbonate, sodium carbonate or sodium hydroxide. Most of the cotton fabrics are dyed with reactive dyes to get high quality shades with good fastness. It is hence imperative to find out the optimum amount of electrolytes required for complete exhaus-

tion of the reactive dyes (Prabu and Sundrarajan, 2002; Makhmatkulova *et al.,* 2002). The present research work was carried out to find the optimum amount of electrolyte which gives maximum dye uptake by the fibre.
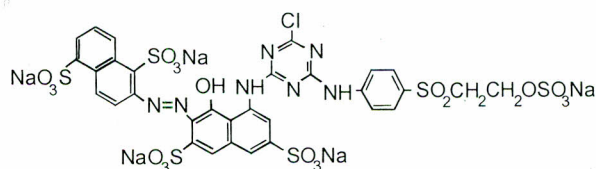
Materials and Methods

Dyes. Two reactive dyes were used in this study:
1. C.I. Reactive Red 240
2. C.I. Reactive Red 241

These dyes were collected from local market. As can be seen from their structure, these dyes are bi-functional in terms of presence of two reactive groups i.e. monochlorotriazine (M.C.T) and vinyl sulfone (VS).
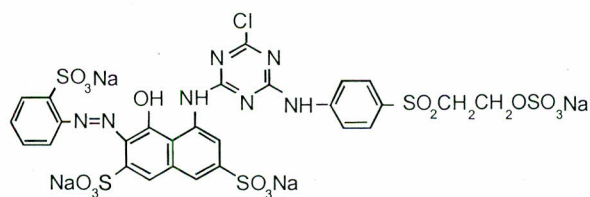
C.I. Reactive Red 240

C.I. Reactive Red 241

Fabric. Degummed and bleached single jersey knitted cotton fabric 180 g/m^2 was used for the study. Prior to dyeing, the cotton fabric was given a mild scouring treatment in a solution containing 2g/l anionic detergent (Lissapol D) for one hour at 50 °C at liquor to goods ratio of 50:1. Scoured fabrics were thoroughly washed in cold water before dyeing.

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Electrolytes used. Sodium chloride, potassium chloride, ammonium chloride, sodium sulphate, potassium sulphate and ammonium sulphate.

Dyeing procedure. To prepare a 0.2% dye solution of C.I. Reactive Red 240, 0.2 g of the dye was dissolved in 50 ml of hot water in order to ensure its solubility, and the volume was made up to 100 ml using tap water. 2 g knitted cotton pieces were weighed and dipped in a beaker containing water (100 ml) and wetting agent (Sandoz Penetrant-EH) (1 ml) for 30 minutes.

Dye solutions (10 ml) was pipetted out in stainless steel beakers separately, and 30 ml of water was added to make the liquor volume up to 40 ml. Temperature of the water bath was adjusted at 65 °C, and the beakers were placed in it. When the solution inside the beakers attained the temperature of 60 °C, squeezed cotton pieces were placed in each beaker and stirred thoroughly for five minutes. Sodium chloride was added to each beaker in quantities of 1 g, 3 g and 5 g, respectively, which are 2.5%, 7.5% and 12.5%, for 1%, 2% and 3% shades, whereas no salt was added for blank reading. After 10 min, 0.4 g sodium carbonate was added to each beaker along with the blank beaker, (used for taking blank reading) with thorough stirring.

The pH and temperature of each dyeing solution was recorded. The dyeing was continued with stirring for one h for 1% shade, 75 min for 2% shade and 90 min for 3% shade stirring. After completion of dyeing process, each fabric was removed, washed with tap water followed by neutral wash with 10% acetic acid and then with boiling water for 60 sec to remove unfixed dye. The dyed cotton pieces were then dried in oven. The same procedure was repeated with two dyes using six electrolytes.

Dyed fabrics were examined using two different colour measuring systems, (1) spectrophotometer model SF600 (USA), (2) model no. Z-Σ 80-II colour measuring system (Japan); the first system used was CIE LAB difference (chroma value and hue) and the second system was CIE chromaticity colour measuring system to select the best dyeing results showed by the electrolytes i.e. sodium chloride, potassium chloride, ammonium chloride, sodium sulphate, potassium sulphate and ammonium sulphate.

For comparison purpose, 36 samples were used which were dyed with the same amount of dye, using the same percentage of different electrolytes. Sodium chloride was taken as standard and others were compared against it. For the fabric sample, which was dyed with C. I. Reactive Red 240, 2.5% concentration of sodium chloride was used as standard and was placed on the sampling port of spectrophotometer, adjusting it as standard; other samples of the same dye with

the same concentration were compared with it. In the same way, for the other fabrics 7.5% sodium chloride was used as a standard and five readings with other five electrolytes (7.5%) were recorded. Then reading with other samples of the C. I. Reactive Red 240 using 12.5% concentration was taken, using 12.5% sodium chloride as standard; observations with other five electrolytes (12.5%) were also recorded. The results obtained in the form of CIE LAB difference are tabulated in Table-1 indicating value (DL*), total colour difference (DE*), chroma (DC*), hue (DH*), redness of colour (Da) and yellow-ness of colour (D6), using the spectrophotometer Model SF 600 (Data Color International), USA. The same procedure was repeated for dyeing of the fabrics with C. I. Reactive Red 240, C. I. Reactive Red 241, using the other five electrolytes; the data of CIE LAB difference is tabulated in Tables 1-4. Three electrolytes, selected from six electrolytes on the basis of their dyeing qualities, assessed through CIE LAB differ-ence, were subjected to CIE chromaticity test using colour measuring system Model Z-Σ 80-II in order to find out the optimum value of concentration of electrolytes giving the best results. The three electrolytes selected were potassium sulphate, sodium sulphate and sodium chloride.

The instrument was adjusted to zero. Then the blank sample of C. I. Reactive Red 240 using (0%) potassium sulphate was placed on the sample port and readings were noted. The same procedure was used with the sample of the same dye and 2.5% potassium sulphate, 7.5% potassium sulphate and 12.5% potassium sulphate to note their CIE chromaticity readings. Readings of the samples dyed with C. I. Reactive Red 240 using sodium sulphate and sodium chloride were noted; results are tabulated in Table 1 and 2. The same procedure was repeated for C. I. Reactive 241 and the results are tabu-lated in Tables 3 and 4.

Results and Discussion

Reactive dyes are mostly used in dyeing of cotton for attractive shades and good fastness. Electrolytes are used to increase the dye uptake by the fibre, which tend to reduce the charge on the fibre considerably, thus facilitating the transfer of dye from solution to the fibre. The concentrations of these electrolytes used were 0%, 2.5%, 7.5% and 12.5%. The fabric used was knitted cotton. Two reactive dyes namely C. I. Reactive Red 240 and C. I. Reactive Red 241 were selected to dye the cotton samples using the above mentioned electrolytes. The CIE LAB difference of these dyed samples were recorded using model SF-600 spectrophotometer USA, where as CIE chromaticity were recorded using Z-Σ-80-II colour measuring system, Japan. 36 dyed samples were examined through SF-600 spectrophotometer for determining

CIE LAB difference by taking sodium chloride as standard and equal concentration of other five electrolytes were compared against the standard and the CIE Lab difference was noted in the form of total colour difference (DE*), chroma (DC*), value (DL*), hue (DH*) redness of colour (Da*) and yellowness of colour (Db*); the results are given in Tables 1-2.

The CIE Lab difference results of Reactive Red 240 (Table 1) show that the order of DE* "the total colour difference" for 2.5 % electrolytes is in the order of potassium sulphate > potassium chloride> ammonium chloride > sodium sulphate > ammonium sulphate. DE* for 7.5% potassium sulphate (5.400) is the highest and for ammonium sulphate (2.176) is the lowest having order potassium sulphate > ammonium chloride > potassium chloride > sodium sulphate > ammonium sulphate. DE* for 12.5% electrolytes is in the order of potassium sulphate (6.721) > potassium chloride (4.871) > sodium sulphate (4.607) > ammonium chloride (4.146) > ammonium sulphate (0.805). For Da* (the redness of colour) the order for 2.5% electrolytes is potassium sulphate (6.009) > potassium chloride (4.715) > sodium sulphate (3.91) > ammonium sulphate (2.121) > ammonium chloride (-1.01). For 7.5% electrolytes the order of Da * is potassium sulphate (4.115) > potassium chloride (2.674) sodium sulphate (2.246) > ammonium chloride (-5.02) ammonium sulphate (-0.28) and for 12.5% electrolytes the order of Da* is the same. The order of Db*(the yellowness of colour) for 2.5% concentration of electrolytes is potassium

sulphate (0.843) > potassium chloride (0.347) > sodium sulphate (-0.17) > ammonium sulphate (-0.74) > ammonium chloride (-1.55). For 7.5% electrolytes, sodium sulphate gives better results as compared to potassium chloride. But with 12.5% electrolytes the order is the same as for 2.5% electrolytes. The order of DC* difference of chroma (the saturation of colour) for 2.5%, 7.5% and 12.5% electrolytes is the same as for Db* . The order of DH*, the depth of shade, for 2.5% and 12.5% electrolytes is the same as for Da* but 7.5% sodium sulphate electrolyte gave better results than potassium chloride. The data of Table 1 shows that 7.5 % concentration of electrolytes is the best for completes exhaustation of the dye. The CIE Lab data of Reactive Red 241 (Table-2) shows that the total colour difference DE* for 2.5 % potassium sulphate is 7.463; for the same concentration of potassium chloride ,it is 6.069 ,for ammonium chloride it is 5.609, for sodium sulphate it is 5.006 and for ammonium sulfate this value is 3.84. Thus for potassium sulphate it is the highest and for ammonium sulphate it is the lowest. The order of DE* for 7.5 % electrolytes is potassium sulphate (7.682) > sodium sulphate (5.993) > potassium chloride (5.325) > ammonium sulphate (4.021) > ammonium chloride (3.053) and 12.5% electrolytes the order of DE* is potassium chloride 2.441. The above data shows that 7.5 % electrolyte is the best for DE*. The order of 2.5% electrolytes for Da* (the redness of colour) is in the order of potassium sulphate (7.746) > potassium chloride (5.389) >

Table 1. CIE Lab difference results of Reactive Red 240 using SF- 600 spectrophotometer

Electrolyte	(%)	DE*	DL*	Da*	Db*	DC*	DH*
KCl	2.5	4.79	0.772	4.715	0.347	4.629	0.961
NH$_4$Cl	2.5	4.729	4.352	-1.01	-1.55	-0.75	-1.69
Na$_2$SO$_4$	2.5	3.925	0.297	3.91	-0.17	3.896	0.366
K$_2$SO$_4$	2.5	6.305	-1.71	6.009	0.843	5.857	1.586
(NH$_4$)$_2$SO$_4$	2.5	3.071	2.093	2.121	-0.74	2.206	-0.43
NaCl	7.5	0	0	0	0	0	0
KCl	7.5	3.086	0.208	2.674	1.528	2.504	1.792
NH$_4$Cl	7.5	3.848	6.964	-5.02	-2.14	-4.66	-2.84
Na$_2$SO$_4$	7.5	2.803	-0.52	2.246	1.593	2.073	1.813
K$_2$SO$_4$	7.5	5.4	-1.44	4.115	3.184	3.826	3.527
(NH$_4$)$_2$SO$_4$	7.5	2.176	2.153	-0.28	-0.15	-0.26	-0.18
NaCl	12.5	0	0	0	0	0	0
KCl	12.5	4.871	-2.72	3.238	2.417	3.015	2.69
NH$_4$Cl	12.5	4.146	5.619	-3.89	-2.09	-3.57	-2.6
Na$_2$SO$_4$	12.5	4.607	-3.14	2.735	1.976	2.543	2.218
K$_2$SO$_4$	12.5	6.721	-3.38	4.364	3.834	4.067	4.148
(NH$_4$)$_2$SO$_4$	12.5	0.805	0.346	0.247	-0.68	0.325	-0.65

DE* = total colour difference; DL* = value; Da* = redness of colour; Db* = yellowness of colour; DC* = chroma; DH* = hue

sodium sulphate (4.534) > ammonium sulphate (1.555) > ammonium chloride (-1.68). Value of Da* for 7.5% electrolytes decreases in the order potassium sulphate (6.512) > sodium sulphate (5.158) > potassium chloride (4.372) > ammonium sulphate (0.698) > ammonium chloride (-0.12) and the value of Da* for 12.5% electrolytes is in the order of potassium sulphate (4.536) > potassium chloride (1.581) > sodium sulphate (1.238) > ammonium chloride (-1.95) > ammonium sulphate (-3.29). The data shows that the best results of Da* are shown by 7.5% electrolytes. The values of Db* (The yellowness of colour) for 2.5% electrolytes are in the order of potassium sulphate > potassium chloride > sodium sulphate > ammonium sulphate. For 7.5% electrolytes the value of Db* is highest for potassium sulphate (3.989) and lowest for ammonium sulfate.(-0.2) and 12% electrolyte this value for potassium sulphate is (3.669) and for sodium sulphate it is 1.228 .This data shows that the best results for Db* are given by 7.5% electrolytes.

Results of Reactive Red 241 (Table 2) for DC* show that the best results are shown by 2.5% potassium sulphate and the poorest by 12.5% ammonium sulphate (-3.4). The value of DC* shown by 7.5% sodium sulphate (6.797) is also compatible. The data for hue of colour DH* is best shown by 7.5% sodium sulphate (3.482) and worst by 12.5% amminium sulphate (-1.97); the results of sodium sulphate (1.228) and potassium chloride (1.139) are compatible. All

the parameters studied by SF–600 spectrophotometer for Reactive Red 240 and reactive Red 241 show that the best results of dyeing are given by three electrolytes i.e. potassium sulphate, sodium sulphate and potassium chloride of 7.5% concentration.

Two electrolytes sodium sulphate and potassium sulphate were selected out of six electrolytes based on the assessment of their dyeing qualities through CIB LAB differences. These two electrolytes were further studied for their CIE chromaticity using Model Z-Σ-80-II Colour Measuring System Japan in order to find out the optimum value of concentration of the electrolytes showing the best results. The CIE chromaticity data is in the form of chroma (C), value (L), hue (H) and Munsell values as tabulated in Tables 3 and 4; graphs, plotted between concentration of electrolytes and chroma value, are given in Fig. 1 and 2. Table 3 for Reactive Red 240 shows that value (L) for 2.5% potassium sulphate is higher as compared to all other concentrations of the same salt and of sodium sulphate. In the same way chroma (C) for 7.5% potassium sulphate has higher value as compared to (C). Value of sodium sulphate gave best saturation of colour. Hue, the depth of colour, is higher for 2.5% potassium sulphate as compared to sodium sulphate. The Munsell value 8.4 RP is higher for 12.5% potassium sulphate as compared to sodium sulphate. In the same way, DL and DE values fo potassium sulphate are greater as compared to the same concentration of sodium

Table 2. CIE Lab difference results of Reactive Red 241 using SF- 600 spectrophotometer

| Electrolyte	(%)	DE*	DL*	Da*	Db*	DC*	DH*
KCl	2.5	6.069	1.621	5.389	2.273	5.484	2.032
NH$_4$Cl	2.5	5.609	5.307	-1.68	-0.7	-1.69	-0.67
Na$_2$SO$_4$	2.5	5.006	0.954	4.534	1.896	4.608	1.708
K$_2$SO$_4$	2.5	7.463	0.051	7.746	3.192	6.904	2.835
(NH$_4$)$_2$SO$_4$	2.5	3.84	3.488	1.555	0.396	1.565	0.353
NaCl	7.5	0	0	0	0	0	0
KCl	7.5	5.325	0.36	4.372	3.017	4.57	2.709
NH$_4$Cl	7.5	3.053	2.99	-0.12	-0.61	-0.14	-0.6
Na$_2$SO$_4$	7.5	5.993	-1.5	5.138	2.658	5.32	2.317
K$_2$SO$_4$	7.5	7.682	-0.83	6.512	3.989	6.797	3.482
(NH$_4$)$_2$SO$_4$	7.5	4.021	3.955	0.698	-0.2	0.689	-0.23
NaCl	12.5	0	0	0	0	0	0
KCl	12.5	2.441	-1.36	1.581	1.272	1.679	1.139
NH$_4$Cl	12.5	3.02	1.362	-1.95	-1.87	-2.05	-1.75
Na$_2$SO$_4$	12.5	2.836	-2.18	1.238	1.238	1.343	1.228
K$_2$SO$_4$	12.5	6.613	-3.12	4.536	3.669	4.878	3.2
(NH$_4$)$_2$SO$_4$	12.5	4.64	2.469	-3.29	-2.15	-3.4	-1.97

DE* = total colour difference; DL* = value; Da* = redness of colour; Db* = yellowness of colour; DC* = chroma; DH* = hue

Table 3. CIE chromaticity results of C.I. Reactive Red 240 using Z-Σ 80-II C system

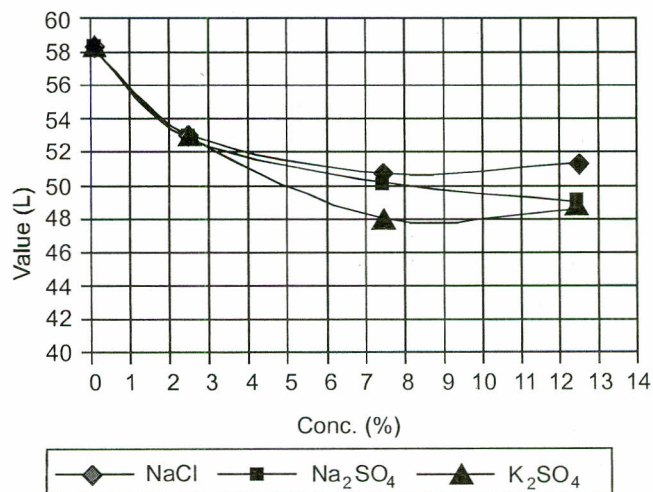| Electrolyte	(%)	L	C	H	Munsell			DL	DE*(ab)
Blank	0	58.25	41.43	353.47	4.78RP	5.65	10.04	51.25	71.48
NaCl	7.5	50.79	52.01	358.99	6.73RP	4.92	12.02	43.69	72.69
NaCl	12.5	51.39	53.13	358.64	6.62RP	4.98	12.33	44.28	73.92
Na_2SO_4	2.5	52.79	51.15	357.24	6.13RP	5.11	11.94	45.67	73.51
Na_2SO_4	7.5	50.13	53.93	0.3	7.16RP	4.87	12.5	43.22	73.75
Na_2SO_4	12.5	48.95	54.89	2.67	7.95RP	4.74	12.69	41.9	73.55
K_2SO_4	2.5	52.96	54.04	359.4	6.80RP	5.13	12.95	45.83	75.66
K_2SO_4	7.5	47.99	57.07	1.92	7.81RP	4.65	13.24	40.97	75.57
K_2SO_4	12.5	48.51	56.05	4.07	8.42RP	4.7	12.95	41.47	74.13

Table 4. CIE chromaticity results of C.I. Reactive Red 241 using Z-Σ 80-II system

Electrolyte	(%)	L	C	H	Munsell			DL	DE*(ab)
Blank	0	64.03	39.82	6.05	8.15RP	6.23	9.68	57.31	75.41
NaCl	7.5	58.32	48.94	9.62	9.12RP	5.64	11.32	52.61	77.34
NaCl	12.5	58.81	46.83	8.41	9.03RP	5.54	11.2	51.34	78.21
Na_2SO_4	2.5	59.61	46.75	7.25	8.74RP	5.79	11.14	52.63	75.76
Na_2SO_4	7.5	57.17	53.75	10.27	9.73RP	5.54	12.52	50.09	78.47
Na_2SO_4	12.5	56.75	51.17	9.61	9.54RP	5.5	11.93	49.66	76.41
K_2SO_4	2.5	59.76	49.18	9.36	9.34RP	5.8	11.64	52.78	77.39
K_2SO_4	7.5	57.26	52.87	11.47	0.05R	5.55	12.28	50.19	77.94
K_2SO_4	12.5	56.54	54.25	13.35	0.7R	5.48	12.48	49.45	78.36
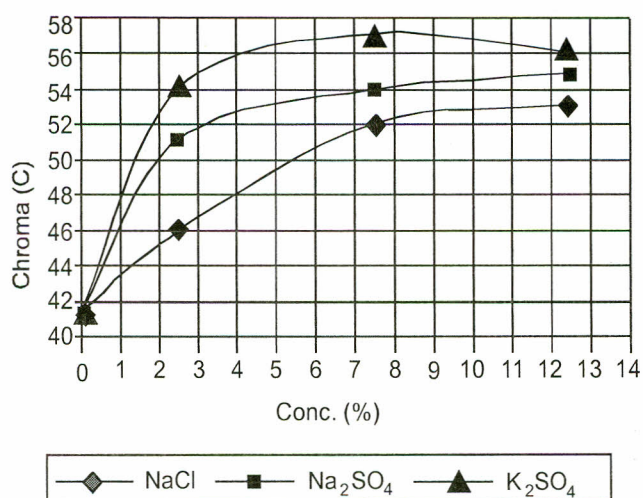
Fig. 1. Concentration of electrolyte versus chroma (C) for C.I. Reactive Red 240.

Fig. 2. Concentration of electrolyte versus value (L) of C.I. Reactive Red 241.

sulphate showing that potassium sulphate is the better electrolyte compared to sodium sulphate. Comparative values of L, C, H, Munsell DL and DE* for Reactive Red 241 (Table 4) shows that the value of L for potassium sulphate is higher than value of L for sodium sulphate. The C value for potassium sulphate is also greater than sodium sulphate .The hue (H) for potassium sulphate is higher than that for sodium sulphate .In the same way Munsell , DL and DE are higher for potassium sulphate as compared to the values for sodium sulphate.

The data shows that potassium sulphate with 7-8% concentration is the best electrolyte for dyeing of Reactive Red 240 and 241 dyes and in some cases, 7-8% concentration gives good results. It is thus concluded that the best dyeing results are given by potassium sulphate and the quality of performance is in the order of potassium sulphate > sodium sulphate > sodium chloride > potassium chloride > ammonium sulphate > ammonium chloride (Makhmatkulova *et al.*, 2002). Ammonium chloride and ammonium sulphate gave poor shades, which may be due to the reason that pH values are 6-8 (low acidic or low basic). Electrolytes more than 8% concentrations do not contribute in dye exhaustion; the excessive amount of electrolyte is drained out and sometimes it gives poor shades due to excessive electrolyte. So this excessive amount of either dye or electrolyte is drained off increasing environmental problems and also the cost of process.

Conclusion

The results obtained are significant as only sodium sulphate showed results comparable to potassium sulphate but the price of sodium sulphate is much less, which makes this electrolyte more favourable. The results obtained are significant; only 7-8% of the electrolyte was sufficient for complete exhaustion for the two dyes used. Thus, a handsome amount of money can be saved by using the required amount of the electrolytes because in large dye houses, huge amounts (in tonnage) of dyes and electrolytes are used.

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