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Alkali-hydrolysis kinetics of alkali-clearable azo disperse dyes containing a fluorosulphonyl group and their fastness properties on PET/cotton blends

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Abstract

The alkali-hydrolysis kinetics of a series of 4-amino-4′-fluorosulphonylazobenzene disperse dyes were investigated using HPLC and their fastness properties on PET/cotton blends were examined. Most of the dyes showed reasonable level of hydrolysis (%) under relatively mild alkaline condition and the dyes having more electron-accepting group in diazo component exhibited lower rate of hydrolysis. The application of fluorosulphonyl containing disperse dyes on PET/cotton blends showed excellent dyeing fastness properties and offers the option of one-bath dyeing process, replacing time- and energy-consuming conventional two-bath dyeing process.

Keywords: Alkali-hydrolysis kinetics; 4-Amino-4′-fluorosulphonylazobenzene; Disperse dye; PET/cotton blends; Dyeing fastness; Alkali clearance; One-bath dyeing

1. Introduction

Since disperse dyes have a limited solubility in water, some particulate disperse dye molecules may still be occluded onto fibre surface after the dyeing is complete. If not removed, this surface contamination can undermine the brightness of shade as well as the wash, sublimation, and rubbing fastness results. The usual treatment carried out is reduction clearing, where the dyed fabric is treated in a strong reduction bath, usually made up of sodium hydrosulphite and caustic soda. However, when the conventional reduction clearing process is applied to azo disperse dyes, azo linkage is broken and, as the case may be, carcinogenic amines are liberated into the effluent, which has high BOD values due to the presence of sodium hydrosulphite [1–3]. Alkali-clearable disperse dyes offer a means of tackling both of these challenges simultaneously. These so-called alkali-clearable disperse dyes obviated the need for sodium hydrosulphite and significantly reduced the cost of effluent treatment [4–6]. Furthermore, it is thought that minimising the need for reduction clearing can lead to substantial productivity improvements and water and chemical savings as well as a reduction on the effluent load and should be a key objective in implementation of a “Rapid Dyeing” approach for polyester [2].

This alkali-clearability is also of particular interest in the dyeing of PET/cotton blends since it enables these dyes to be applied in the same bath with cotton reactive dyes for a one-bath, two-step dyeing process. Any superficial disperse dye on the PET or any disperse dye cross-staining on the cotton is hydrolysed, dissolves and washes off while reactive dye is exhausted onto the cotton.

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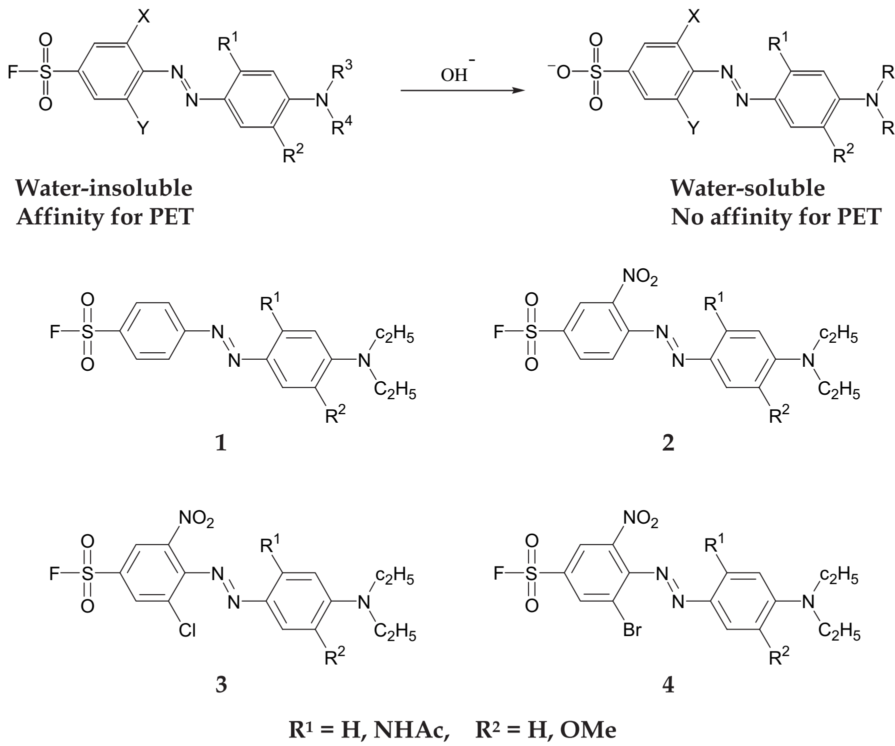


Scheme 1. Alkali-hydrolysis of 4-amino-4′-fluorosulphonylazobenzene disperse dyes (X,Y = H, Cl, Br, NO_2, R^1, R^2 = H, CH_3, OCH_3, $NHCOCH_3$, R^3, R^4 = substituted alkyls).

Therefore, by incorporation of an alkali clearing stage, in addition to the improved productivity, we can anticipate high levels of wash fastness even in heavy depths [6].

In previous work [7–15], we suggested novel alkali-clearable azo disperse dyes containing a sulphonyl fluoride group. The azo disperse dyes containing a fluorosulphonyl group were hydrolysed under alkaline condition by S_N2 mechanism (Scheme 1), and pseudo first-order kinetics were determined by analysis of the dye hydrolysis under alkaline conditions using HPLC [7–9]. Their spectral properties were also examined with respect to the effects of substituents in absorption spectra, halochromism and solvatochromism [11].

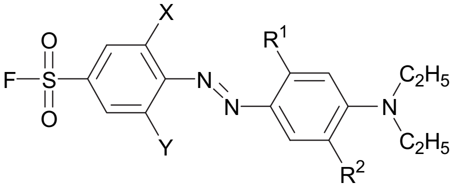
In this study, we reported the alkali-hydrolysis kinetics of monoazo disperse dyes containing a fluorosulphonyl group, 4-(*N*,*N*-diethylamino)-4′-fluorosulphonylazobenzene derivatives (**1–4**) under mild alkaline condition as well as the fastness properties on PET/cotton blends.

2. Experimental

2.1. Materials

PET/cotton fabrics (PET:cotton = 65%:35%, Twill weave, warp: 136 threads/inch, weft: 72 threads/inch) were used for dyeing throughout the study. All the chemicals used in the synthesis, HPLC analysis and dyeing were of laboratory-reagent grade. Diwatex (Borregaard Ligno Tech, anionic) was used as a dispersing agent for milling and Lyocol RDN Liquid (Clariant, anionic) was used as a dispersing agent for the dyeing of polyester fabric. Sandozin NIE (Clariant, nonionic) was used as a wetting agent.

Table 1
4-(*N*,*N*-diethylamino)-4′-fluorosulphonylazobenzene dyes (**1–4**) used in the present study



Dye	X	Y	R^1	R^2	λ_{max} (EtOH, nm)
1a	H	H	H	H	469
1b	H	H	CH_3	H	478
1c	H	H	$NHCOCH_3$	OCH_3	519
2a	NO_2	H	H	H	513
2b	NO_2	H	CH_3	H	524
2c	NO_2	H	$NHCOCH_3$	OCH_3	573
3a	NO_2	Cl	H	H	520
3b	NO_2	Cl	CH_3	H	539
3c	NO_2	Cl	$NHCOCH_3$	OCH_3	595
4a	NO_2	Br	H	H	522
4b	NO_2	Br	CH_3	H	542
4c	NO_2	Br	$NHCOCH_3$	OCH_3	594

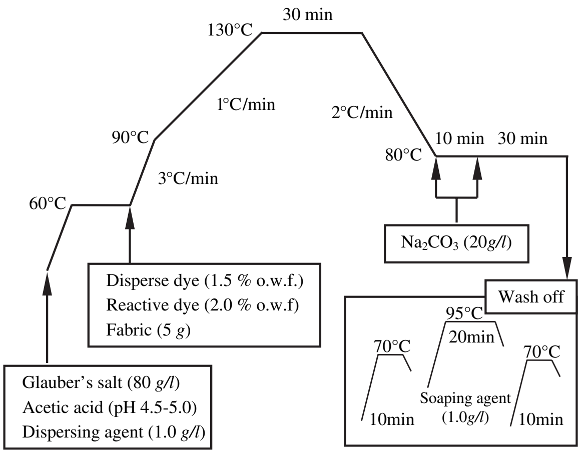


Fig. 1. One-bath dyeing profile of PET/cotton blends.

2.2. Dye synthesis

The synthesis of 4-(*N*,*N*-diethylamino)-4′-fluorosulphonylazobenzene disperse dyes has been described in the previous paper [10]. The dyes (**1–4**) that were used throughout the study were given in Table 1.

2.3. Alkali-hydrolysis analysis

Alkaline hydrolysis kinetics was investigated at the alkali (Na_2CO_3) concentration of 20 g/l and the temperature of 80 °C in order to confirm the feasibility of the one-bath dyeing of PET/cotton blends using the synthesised dyes.

The dye liquors were prepared by dispersing 0.02 g of formulated dyes in 200 ml of buffer solution preheated

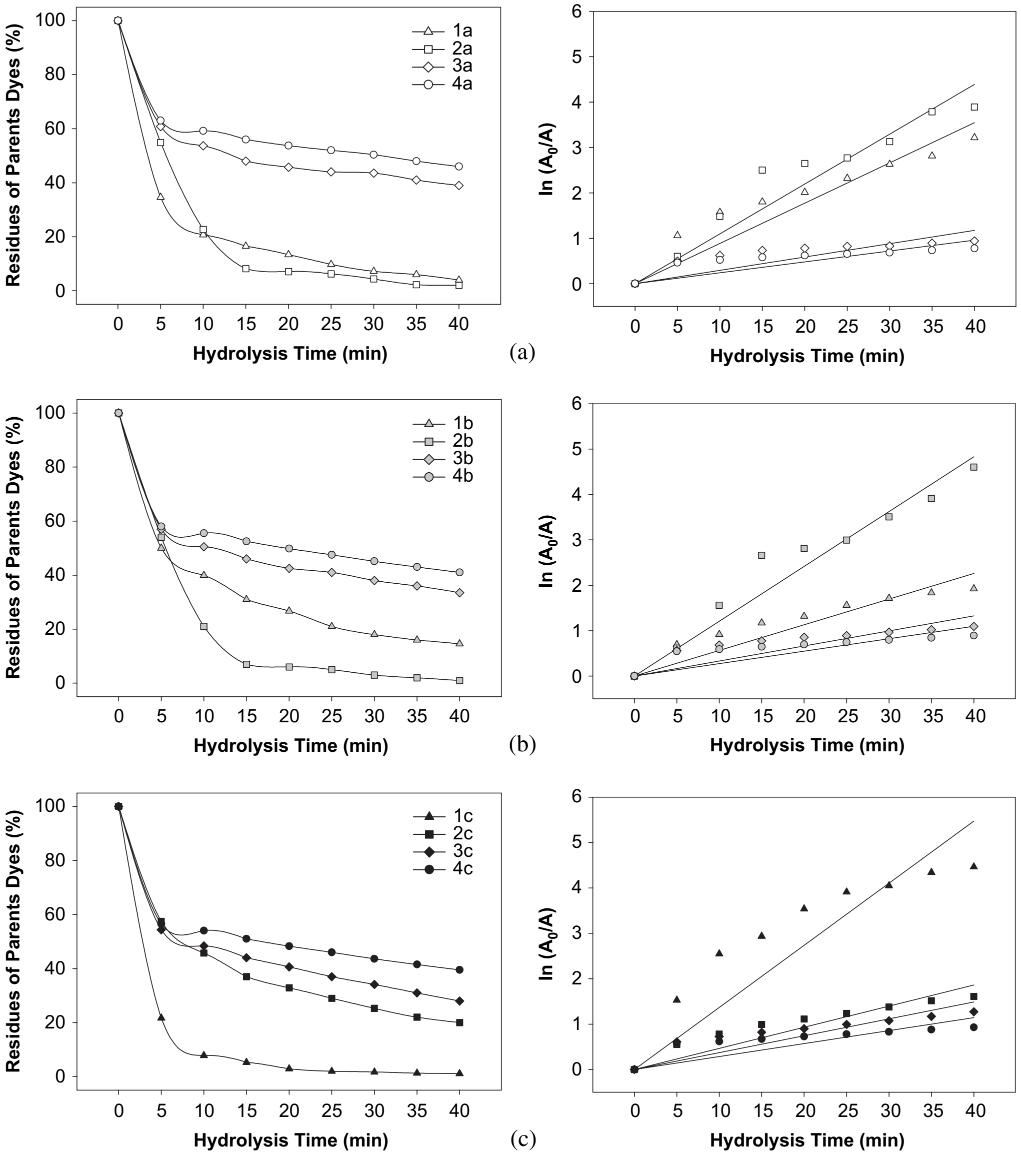


Fig. 2. Alkali-hydrolysis behaviours of **1–4** under alkaline condition (Na_2CO_3, 20 g/l, 80 °C) (a) **1a–4a**; (b) **1b–4b**; (c) **1c–4c**.

to proper temperature in water bath. The dye liquor was stirred at the temperature for 50 min and 2 ml aliquots were withdrawn from the dye solution at 5 min intervals and immediately neutralised to pH 4.0–4.5 with equivalent amounts of dilute HCl and cooled to prevent further hydrolysis reactions. Ten millilitres of acetonitrile was added into each withdrawn samples to prepare sample of proper composition (acetonitrile:water = 80:20) for HPLC analysis. Analysis was carried out at room temperature using a HPLC (Varian 5000 Liquid Chromatograph, USA, Varian) with a C18 reverse-phase column and a mixture of acetonitrile and deionised water was used as the mobile phase. Ten microlitres of samples were injected to be analysed, and were detected at the wavelength of absorption maxima (λ_{max}).

2.4. Dyeing

PET/cotton blend fabrics were dyed in a laboratory dyeing machine at a liquor ratio of 30:1. The dyeing of polyester/cotton blends was carried out using both conventional two-bath dyeing method and one-bath, two-step dyeing method. In the conventional two-bath dyeing, polyester component was dyed in 1st bath by the general polyester dyeing method (130 °C, 30 min) and cotton component was dyed in 2nd bath by the general reactive dyeing method (80 °C, 70 min). In the one-bath, two-step dyeing method, both disperse dye for polyester and reactive dye for cotton are introduced at the start of the dyeing. The polyester component was dyed first at 130 °C, then alkali was added after the temperature of the dyebath cooled down to 80 °C (Fig. 1).

2.5. Fastness test

A proportion of the dyed fabrics were stentered at 180 °C for 30 s. 1/1 Standard depth was chosen for the fastness test in order to secure optimum fastness of the dyeing to washing. The colour fastness was determined according to International Standards ISO 105 C06/C2S (fastness to washing). These fastness tests were examined for one-bath, two-step process and two-bath process in order to measure the suitability of the synthesised dyes for one-bath dyeing of PET/cotton blends, respectively. Staining and change in colour were assessed using grey scales.

3. Results and discussion

3.1. Alkali-hydrolysis kinetics

Sulfonyl halide can be hydrolysed to the corresponding acid by nucleophilic bimolecular substitution (S_N2) mechanism under alkaline condition [16,17]. Therefore, it is presumed that azo disperse dyes containing a fluorosulphonyl group can be hydrolysed under alkaline condition by S_N2 mechanism shown in Scheme 1.

Considering that addition of hydroxide ion to the electrophilic sulphur atom is the rate-determining step of the hydrolysis reaction, and that hydroxide ion concentration is kept constant by the use of a buffer or large excess of alkali, the rate of concentration decrease of parent dye in the alkaline solution can be expressed by Eq. (1) [18]:

$$-\frac{d[P]}{dt} = k_{ps1}[P] \qquad (1)$$

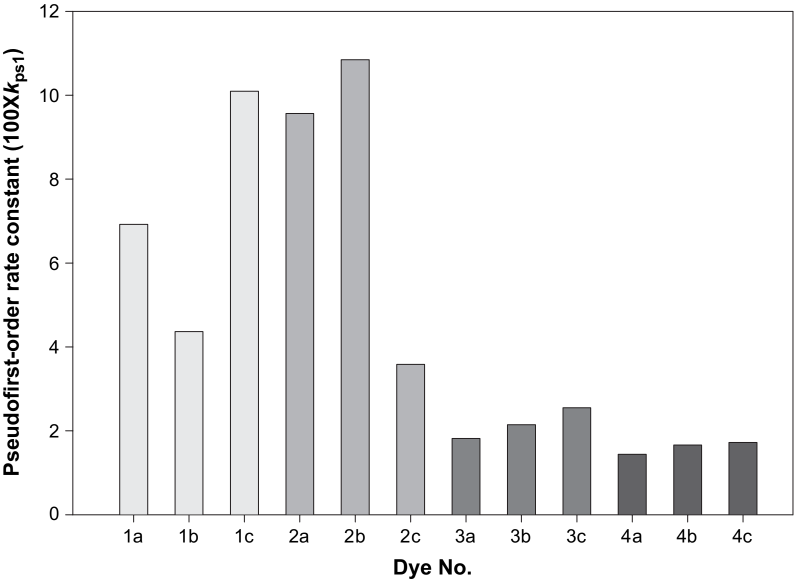


Fig. 3. Pseudo first-order rate constants of the dyes **1–4** under alkaline condition (Na_2CO_3, 20 g/l, 80 °C).

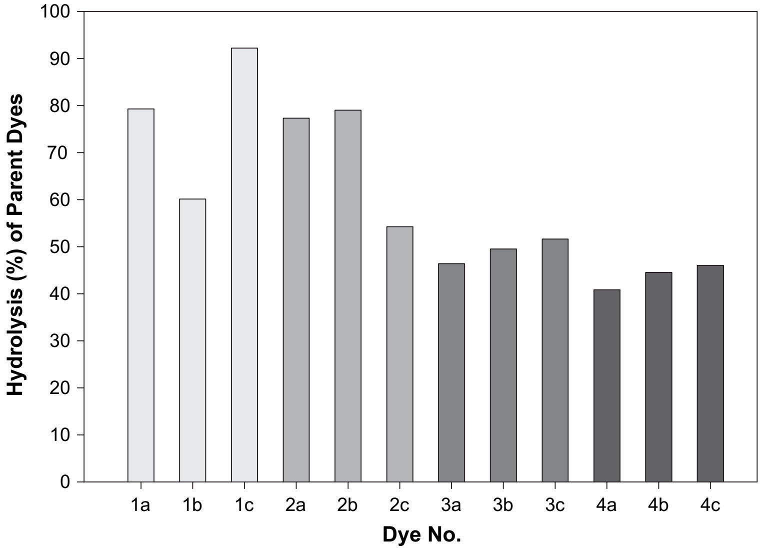
in which $[P]$ is the concentration of the parent dye at hydrolysis time t, and k_{ps1} is the pseudo first-order rate constant of hydrolysis. The values of the peak areas of the components determined from the chromatograms are linearly related to their amount. Replacement of the concentrations of the parent dye with peak areas leads to Eq. (2).

$$\ln\left(\frac{A_0}{A}\right) = k_{ps1}t \quad (2)$$

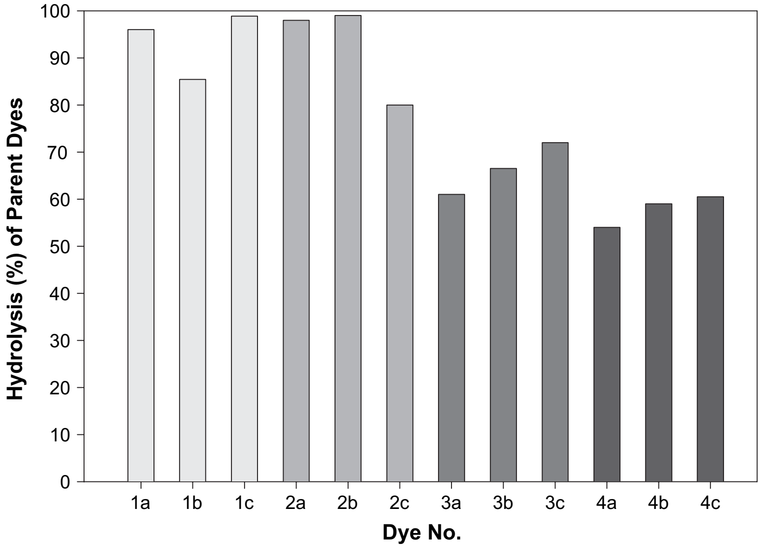
where A_0 and A are values of peak areas of the parent dye at the time $t = 0$ and at a later time t. This equation shows that if $\ln(A_0/A)$ is plotted against t, then a first-order reaction will give a straight line [19].

In order to estimate the suitability of 4-amino-4′-fluorosulphonylazobenzene disperse dyes for the one-bath dyeing of PET/cotton blends, the hydrolysis analysis of the disperse dyes containing a fluorosulphonyl group was carried out at the alkali (Na_2CO_3) concentration of 20 g/l and the temperature of 80 °C. Hydrolysis was monitored every 5 min for 40 min since usually 40 min is necessary for the dyeing of cotton fibre in one-bath dyeing process of PET/cotton blends (Fig. 1).

Hydrolysis behaviour of dyes at 80 °C under the alkaline condition (Na_2CO_3, 20 g/l) was shown in Fig. 2. It shows the expected exponential decrease in the amount of parent dye with increasing hydrolysis time and the plot of $\ln(A_0/A)$ against time t yields a straight line. However, the correlation coefficients of the



(a)



(b)

Fig. 4. Hydrolysis (%) of parent dyes **1–4** after (a) 10 min and (b) 40 min under alkaline condition (Na_2CO_3, 20 g/l, 80 °C).

hydrolysis using Na_2CO_3 was relatively lower than that using NaOH of previous work, probably because the alkali concentration is not excess enough for the approximation of pseudo first-order equation [7–9,18].

According to Eq. (2), the expected pseudo first-order kinetics was confirmed (Fig. 2) and the slope of the plot was calculated to determine the pseudo first-order rate constant k_{ps1}. Fig. 3 shows the determined pseudo first-order rate constants of synthesised dyes under alkaline condition (Na_2CO_3, 20 g/l) and temperatures (80 °C).

Taking a closer look reveals that the dyes having more electron-accepting group in diazo component showed lower rate of hydrolysis; however, no clear relationship between the electron-donating power of substituents in coupling components and hydrolysis rate was found [8,9].

Fig. 4 shows the hydrolysis (%) of parent dyes after 10 min and 40 min under alkaline condition (Na_2CO_3, 20 g/l) and temperatures (80 °C). Dyes **1** and **2** hydrolysed over 80% at mild alkaline condition while dyes **3** and **4** showed relatively lower hydrolysis (%) values (59–72%). Assuming that more than 80% hydrolysis (%) is required to guarantee good fastness and that the holding time after alkali-addition is about 40 min in one-bath dyeing of PET/cotton blends, then it seems that the rate of hydrolysis of dyes **1** and **2** is high and sufficient alkali clearance occurs even under mild alkaline condition (Na_2CO_3, 20 g/l).

3.2. Fastness properties

The fastness of polyester dyeings of dyes **1–4** was examined in an attempt to assess whether the presence of the fluorosulphonyl function conferred the property of alkali-clearability. These fastness tests were examined for one-bath, two-step process and two-bath process, respectively.

The synthesised dyes containing a fluorosulphonyl group showed excellent levels of wash fastness using the ISO 105 C06/C2S. Figures for wash fastness of the dyed fabrics are shown in Table 2. The fastness of one-bath dyed fabric was similar to that of two-bath dyed fabric, and both showed high levels of fastness, presumably because the fluorosulphonyl group of the synthesised dyes is hydrolysed in alkali to solubilising sulphonate group as was investigated in previous study [7–9]. These alkali-clearable dyes are therefore readily removed by alkali-addition in one-bath dyeing, and exhibit low staining in wash fastness tests. Dyes **3** and **4**, which have relatively lower hydrolysis rate also showed excellent wash fastness, irrespective of the dyeing method. The results indicate that, with these synthesised disperse dyes containing a fluorosulphonyl group, one-bath dyeing process can be used instead of conventional two-bath dyeing process just as effectively. Nylon and diacetate were consistently the most stained components of the multifibre, presumably because of the combination of the dye's substantivity for these materials and the fibres' accessibility at the test temperatures. While the dyes are substantive to polyester and acrylic, diffusion of the dyes into these materials at the test temperature is low and, consequently, staining was less pronounced than that with the nylon and diacetate. Also, the hydrophilicity of cotton ensures that it was stained least.

4. Conclusions

Azo disperse dyes incorporating a fluorosulphonyl group hydrolysed under relatively mild alkaline conditions and temperature. The hydrolysis of 4-amino-4′-fluorosulphonylazobenzene disperse dyes in alkaline solution at constant temperature followed pseudo first-order kinetics. The dyes having more electron-accepting

Table 2
Fastness to washing of dyes **1–4** (ISO 105 C06 C2S, 1/1 standard depth)

Dye	Change		Staining											
	One-bath	Two-bath	One-bath						Two-bath					
			W[a]	A[b]	P[c]	N[d]	C[e]	D[f]	W	A	P	N	C	D
1a	5	5	4	5	5	3–4	4–5	4	4	5	4–5	3–4	5	4
1b	4–5	5	4	5	4–5	3	4–5	3	4	5	4–5	3	4–5	3–4
1c	5	5	4	5	5	4	4–5	4	4	5	5	4	4–5	4
2a	5	4–5	4–5	5	5	4–5	4–5	4–5	5	5	5	4–5	5	5
2b	4–5	4–5	4	5	5	4–5	4–5	4–5	4	5	5	5	5	4–5
2c	4–5	4–5	4–5	5	5	4–5	4–5	4–5	4–5	5	5	4–5	5	4–5
3a	4	4	4–5	5	5	4–5	5	5	5	5	5	5	5	5
3b	4–5	4–5	4	5	5	4	4–5	4–5	4	5	5	4	5	4–5
3c	4–5	4–5	4	5	5	4–5	5	5	4–5	5	5	4–5	5	5
4a	4	4	4–5	5	5	4–5	5	5	4–5	5	5	5	5	5
4b	4	4–5	4	5	5	4	4–5	4–5	4	5	5	4	5	4–5
4c	4–5	4–5	4	5	5	4–5	5	5	4–5	5	5	4–5	5	5

W[a]: Wool; A[b]: Acetate; P[c]: PET; N[d]: Nylon; C[e]: Cotton; D[f]: Diacetate.

group in diazo component were showed lower rate of hydrolysis; however, no clear relationship between the electron-donating power of substituents in coupling components and hydrolysis rate was found.

The synthesised dyes containing a fluorosulphonyl group showed excellent levels of wash fastness in one-bath dyeing of PET/cotton blends, probably because their alkali-clearable property enables the dyes to be applied in the same bath with cotton reactive dyes for a one-bath, two-step dyeing process. Any superficial disperse dye on the PET or any disperse dye cross-staining on the cotton is hydrolysed, dissolves and washes off while reactive dye is exhausted onto the cotton. Therefore, by incorporation of an alkali clearing stage, in addition to the improved productivity, we can anticipate high levels of wash fastness even in heavy depths. Therefore, in addition to the improved productivity over the conventional two-bath dyeing method, we can achieve high levels of wash fastness even in heavy depths by the incorporation of an alkali clearing stage.

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