KINETIC STUDY OF HYDROLYSIS OF REACTIVE DYE USING HPLC

Anjum Ahmad[1]*, Ashok Athalye[2], S.R. Shukla[3]

[1]M.Tech, Dept. of Fibres and Textile Processing Technology, Institute of Chemical Technology, Mumbai, India.
[2]Professor, Dept. of Fibres and Textile Processing Technology, Institute of chemical Technology, Mumbai, India.
[3]Ex-professor, Dept. of Fibres and Textile Processing Technology, Institute of chemical Technology, Mumbai, India.

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Abstract - *High Performance Liquid Chromatography (HPLC) has the ability to separate out and quantitatively identify compounds that are present in any solution. Kinetic study of hydrolysis of Procion Blue H-EGN (Colour Index Generic name: Reactive Blue 198 | CAS number: 124448-55-1) was performed using a C-18 reverse-phase HPLC. Gradient method was employed by a solvent. Solvent A (100% acetonitrile containing 0.025M tetrabutylammonium bromide) was used as an ion pairing agent and solvent B (30 parts of A and 70 parts of deionized water containing 0.05M ammonium dihydrogenphosphate) as a mobile phase.*

Key Words: **C. I. Reactive Blue 198, Hydrolysis, Kinetic study, High-performance liquid chromatography (HPLC), UV-Visible spectrophotometer.**

1. INTRODUCTION

Cotton is mainly dyed with Reactive, Vat, Direct and Sulphur dyes. Reactive and Vat dyes occupy the major share, of which highest volume is that of Reactive dyes owing to their ease of application, ample shade gamut, bright shades, all round fastness properties and lower cost.

Bi-functional dyes have more than one type of reactive systems. It may be homo or hetero-functional group.

Sodium carbonate is used as an alkali to maintain pH between 10.5 and 11.5 for the formation of cellulosate ions in cotton cellulose that make covalent bonds with reactive dyes (Lewis, 2009). However, hydrolysis of the dye occurs simultaneously at this pH. A reactive dye, which is capable of reacting with cellulosate ion can certainly react with hydroxyl ion of water. In a reactive dyeing process, therefore, two competing reactions proceed simultaneously.

Dye-X + H+ -O-Cell → Dye-O-Cell + HX   (1)

Dye-X + H+ -OH → Dye-OH + HX   (2)
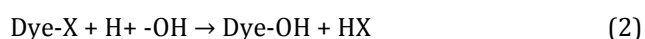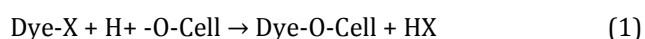
(X= any reactive group)

The first reaction is the desired one leading to dye fixation on cotton material, while the second is a side reaction leading to the formation of an inactive hydroxyl derivative of the dye.

The hydrolyzed dye does not react with cotton but is held only substantively like direct dyes, leading to poor wash fastness. A large volume of water is required to remove the hydrolyzed dye in a subsequent wash-off process of dyed material, to achieve desirable fastness properties (Shah, 2010). Reactive dyeing process thus leads to high volumes of coloured waste water due to discharge of highly colored dye bath along with higher electrolyte concentration.

The study of hydrolyzed reactive dye by HPLC is a technique, wherein a mixture of hydrolyzed and unhydrolyzed dyes is separated quantitatively. Separation of components of the mixture is based on adsorption in the column and desorption from column followed by a partition which is recorded by the detector. Adsorption of elements depends upon the polarity of the component. Each element has different polarity, so they adsorb at various positions of the column and desorb according to the adsorbed position. The first adsorbed component gets desorbed first, and its peak will appear first. Consequently, different peaks are detected at different positions, making it possible to identify the components of hydrolysis reaction based on their retention time, i. e., the time taken by a particular compound to elute from the column after injection (http://www.chem.agilent.com).

The measurement of the quantity of a compound in a sample may be achieved by interpretation of the chromatogram, by height or area under the peaks, taking total height or total area as 100 percent (http://polymer.ustc.edu.cn).

2. Experimental

2.1 Dye

The dye Procion Blue H-EGN (C. I. Reactive Blue 198) was procured as a commercial sample from Atul Ltd
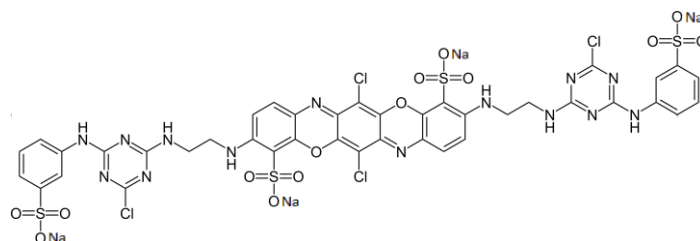

Figure -1: C. I. Reactive Blue 198

2.2 Chemicals

All chemicals were HPLC grade obtained from SD Fine Chemicals Ltd.

Table 2.1: Chemicals used in HPLC

Chemical	Used as	Chemical structure
Acetonitrile	mobile phase	H—C—C≡N (with H atoms shown)
Tetrabutylamm onium bromide	ion pairing agent	H_3C ... CH_3 ... N^+ ... H_3C ... CH_3 ... Br^-
Deionised water	mobile phase	H_2O
Ammonium dihydrogen phosphate	buffer	$HO-\overset{O}{\underset{HO}{P}}-O^-\ NH_4^+$
Methanol	mobile phase	H—C—O—H (with H atoms shown)

2.2 Experimental procedures

Study of hydrolysis was carried out with following parameters:

Table -2.2: Dyeing conditions

Dye	Temperature , °C	Shade , %	Na_2SO_4, g/l	Na_2CO_3, g/l
C. I. Reactive Blue 198	80	0.5	15	5
		1.0	20	10
		2.0	25	15

Process

(i) Sample preparation

Dye baths containing aqueous solutions of the dye, C. I. Reactive Blue 198, were prepared for 0.5%, 1% and 2% shades owf with MLR 1:40, alkali and salt [Reference Table-2.2]. Ten ml solution was withdrawn from the dye bath each at the intervals of 0, 25, 45, 55, 65, 75, 85, 95, 105 min into a 25 ml volumetric flask and immediately neutralized to pH 7 with 0.1N HCl to prevent further hydrolysis of the dye. The aliquots were diluted with deionized water up to the mark. The solution was filtered through Whatman, 10414112 (0.45 µm pore size) filter paper. The injected volume of each analyzed sample was 20 µl (Dordevic et al., 2006).

(ii) HPLC analysis

The analysis was carried out at room temperature using HPLC with a C-18 reverse-phase (and capped, 5 µm) column of 250×4.6 mm. Gradient elution was used with solvent A (100% acetonitrile containing 0.025 M tetrabutylammonium bromide) as an ion pairing agent and solvent B (30 parts of A and 70 parts of deionized water containing 0.05M ammonium dihydrogen phosphate) as a mobile phase. With the flow rate of the mobile phase at 1 ml/min, 20 µl of neutralized dye

solution was injected. Separated unhydrolyzed and hydrolyzed dyes, eluted from the column, were detected at wavelengths of 592 nm. Gradient eluent means the variable concentration of solvent A and B flow with respect to time.

(iii) Gradient method for mobile phase

Table 2.3: Mobile phase composition changing with time for Gradient method

Time, min	Solvent A, %	Solvent B, %
0	30	70
5	40	60
10	50	50
15	30	70

3. Results & discussion

Percentage of the hydrolyzed dye was obtained directly from the peak height of the HPLC output as the percentage height, for the dye C. I. Reactive Blue 198 at different shades.

Rate constant was calculated by pseudo-first order rate of reaction

$$-\frac{d[Ct]}{dt} = kt$$

Where, Ct is the dye concentration at a given time, and k is the rate constant, k saw the rate of decrease in concentration in a unhydrolyzed dye which will be equal to increase in the concentration of hydrolyzed dye, so k value gave the rate constant of hydrolyzed dye.
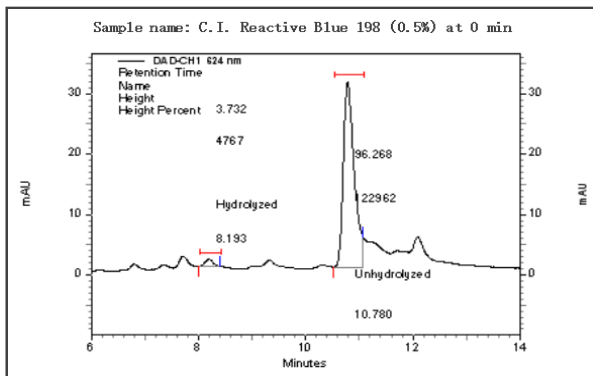
By integrating, taking concentration at t=0 was Co and at t=t was Ct, the equation becomes
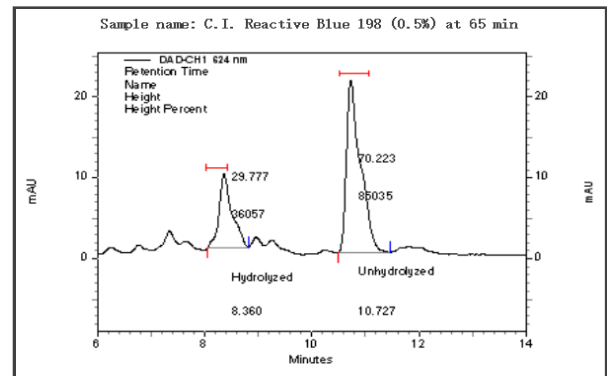
log Ct= -kt + log Co

Plotting the graph between log Ct 'vs' time, found a straight line and slope of this line gave the rate constant of hydrolyzed dye.

The peak value of HPLC shown in Figures (3.1, 3.4, 3.7), where hydrolyzed dye's peak shown before a unhydrolyzed peak because hydrolyzed dye contain –OH group which have more polarity than all halide reactive group. Those molecules which have more polarity will absorb first at C18 reverse phase Column and detect first, so the peak of hydrolyzed is shown before the unhydrolyzed dye and the same character was shown in all the concentrations of reactive dye.
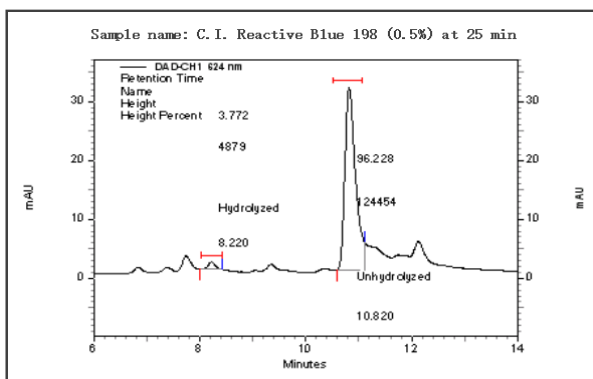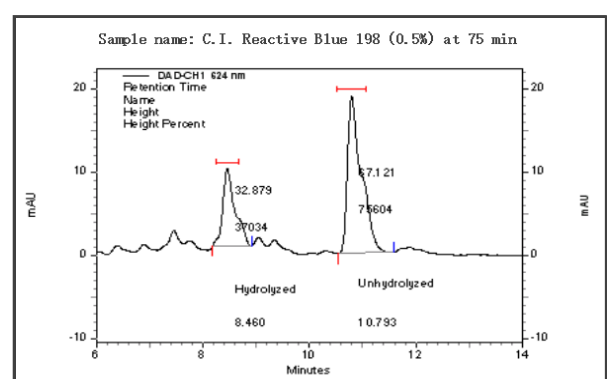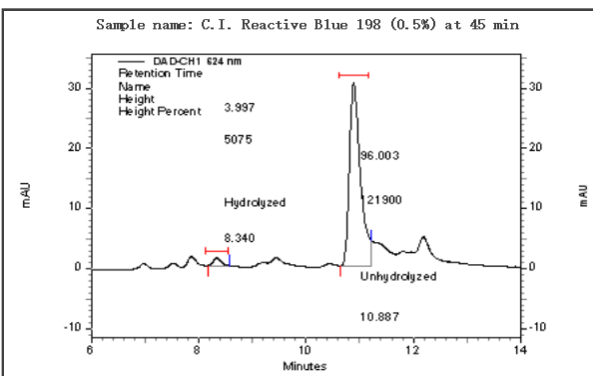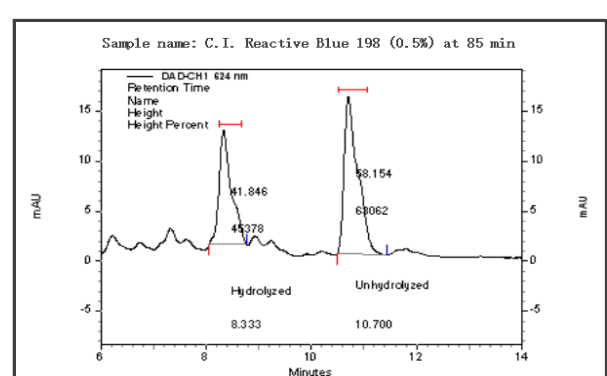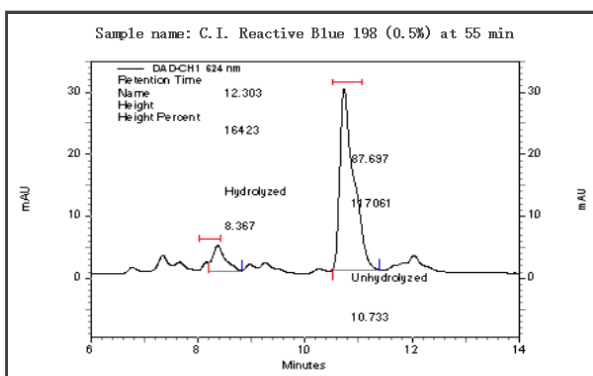
HPLC Result of C.I. Reactive Blue 198 0.5%

(A)

(E)

(B)

(F)

(C)

(G)

(D)

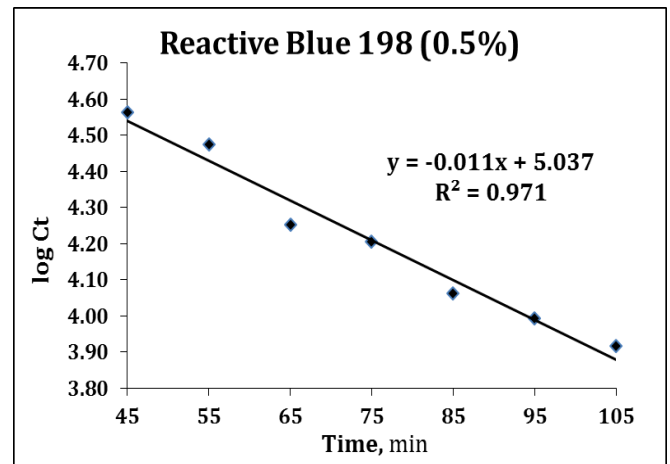

(H)

(I)

Figure -3.1: HPLC Result of C. I. Reactive Blue 198 dyes 0.5% (A) 0 min (B) 25min (C) 45min (D) 55min (E) 65min (F) 75min (G) 85min (H) 95min (I) 105min.

Table -3.1: Extent of hydrolysis of C. I. Reactive Blue 198 0.5% at different time

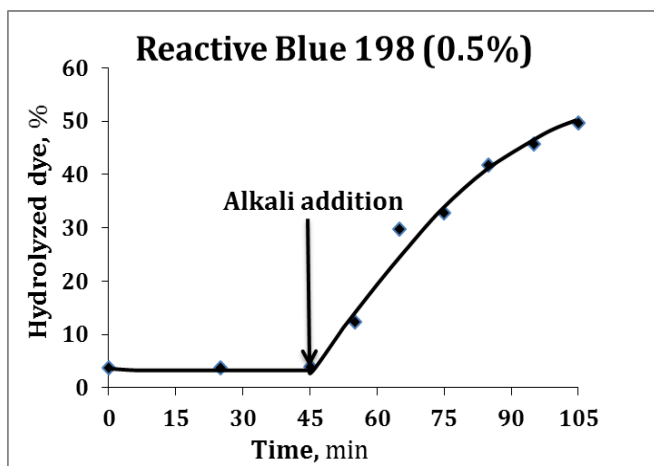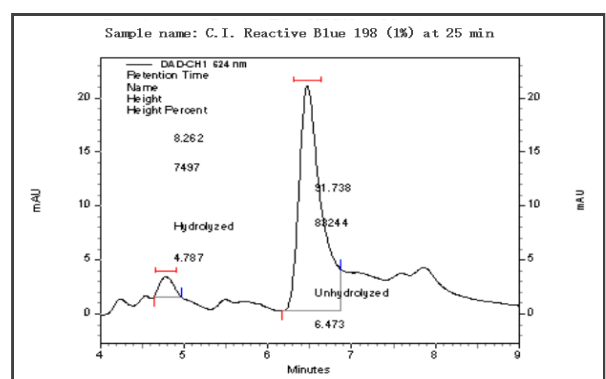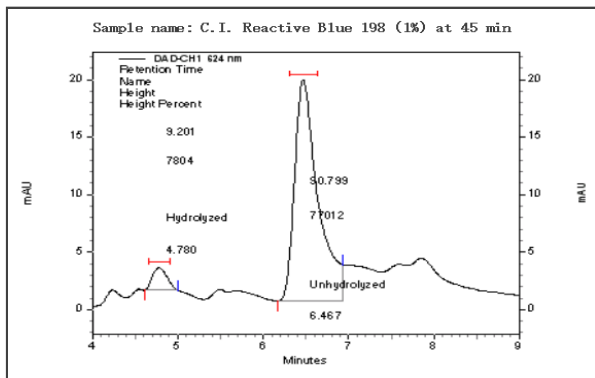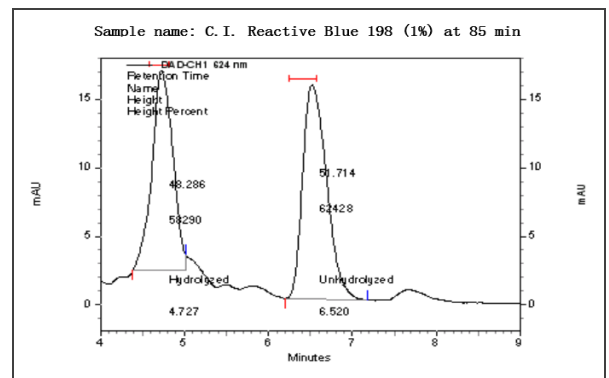| Time, min	Unhydrolyzed dye, %	Hydrolyzed dye, %	log Ct	Rate constant, min^{-1}
0	96.27	3.73	4.57	
25	96.23	3.77	4.57	
45	96.00	4.00	4.56	
55	87.70	12.30	4.47	
65	70.22	29.78	4.25	0.011
75	67.12	32.88	4.21	
85	58.15	41.85	4.06	
95	54.22	45.79	3.99	
105	50.30	49.71	3.92	
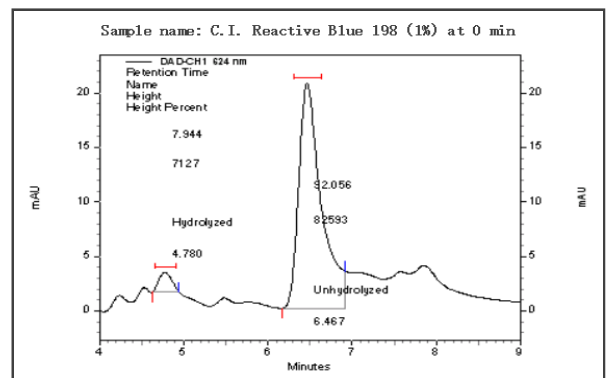
Figure -3.2: Relation between amount of hydrolyzed dye and time of treatment for C. I. Reactive Blue 198 (0.5%)

Figure -3.3: Relation between log Ct and time after addition of alkali to the dye bath for C. I. Reactive Blue 198 (0.5%)

HPLC Result of C. I. Reactive Blue 198 1%
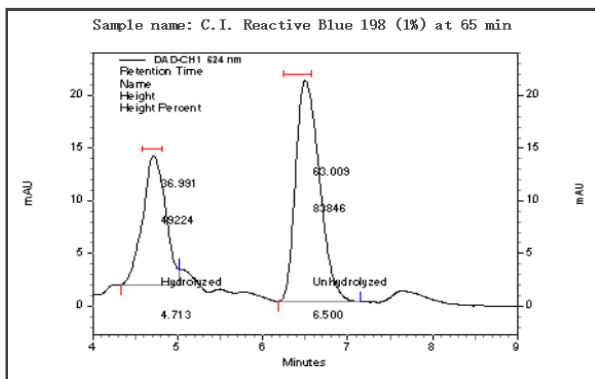

(A)
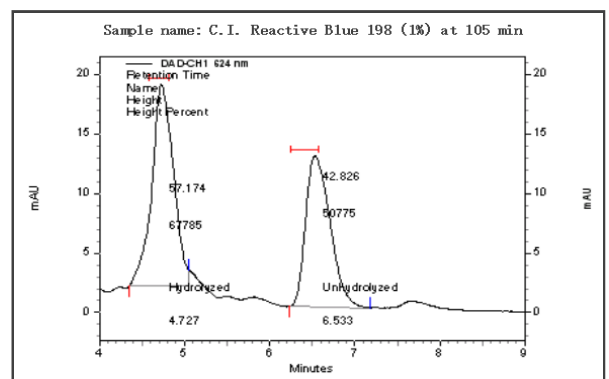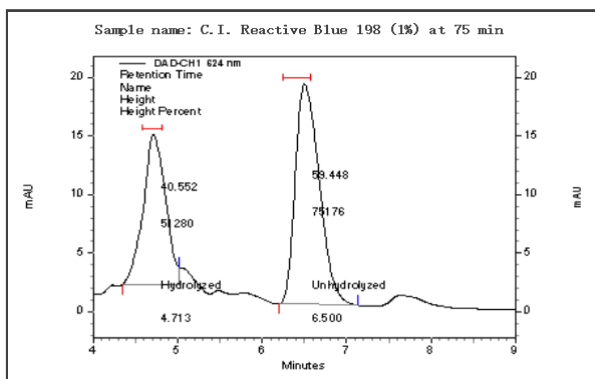

(B)

(C)

(D)

(E)

(F)

(G)

(H)

(I)
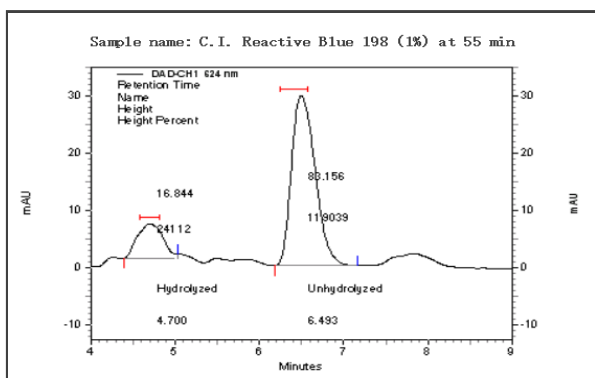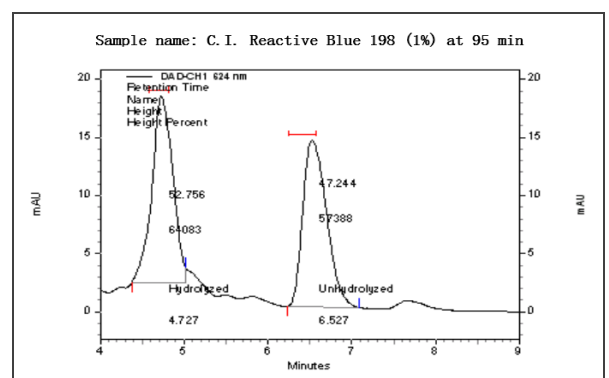
Figure -3.4: HPLC Result of C. I. Reactive Blue 198 dyes 1% (A) 0 min (B) 25min (C) 45min (D) 55min (E) 65min (F) 75min (G) 85min (H) 95min (I) 105min.

Table -3.2: Extent of hydrolysis of C. I. Reactive Blue 198 1% at different time

Time, min	Unhydrolyzed dye, %	Hydrolyzed dye, %	log Ct	Rate constant, min⁻¹
0	92.06	7.94	4.52	
25	90.37	9.63	4.50	
45	90.37	9.63	4.50	
55	83.16	16.84	4.42	
65	63.01	36.99	4.14	0.012
75	59.45	40.55	4.09	
85	51.71	48.29	3.95	
95	47.24	52.76	3.86	
105	42.83	57.17	3.76	

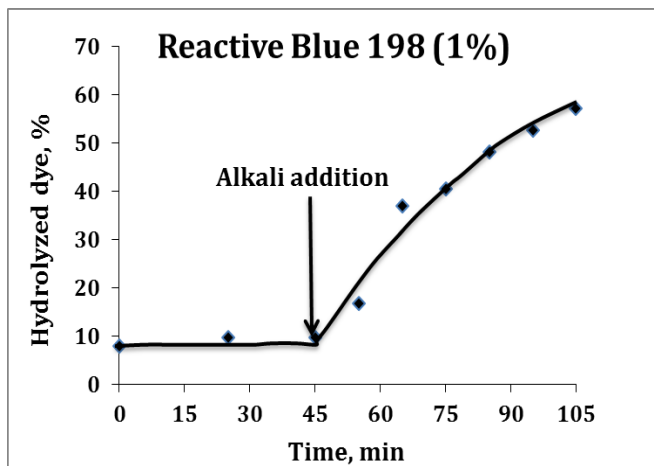**HPLC Result of C. I. Reactive Blue 198 2%**

(A)

(B)

Figure -3.5: Relation between amount of hydrolyzed dye and time of treatment for C. I. Reactive Blue 198 (1%)
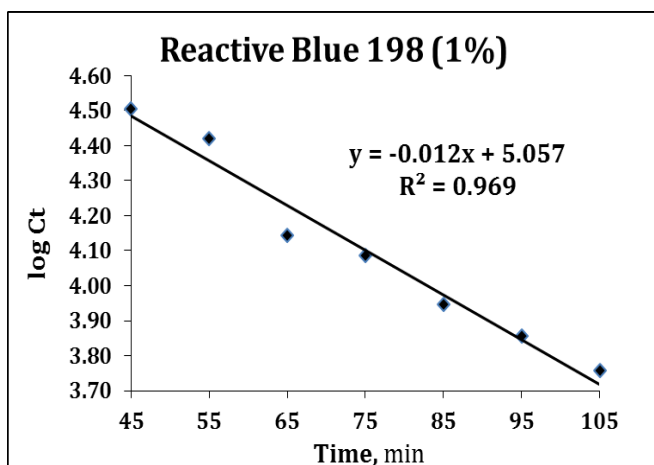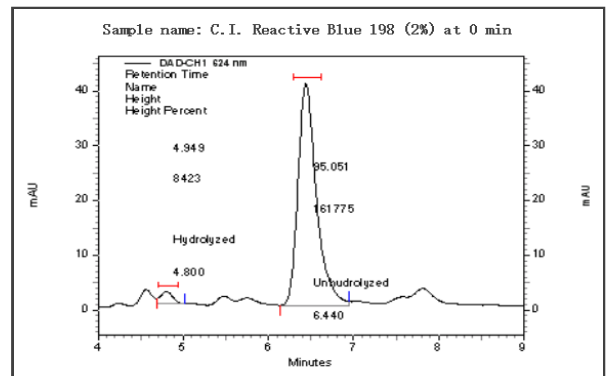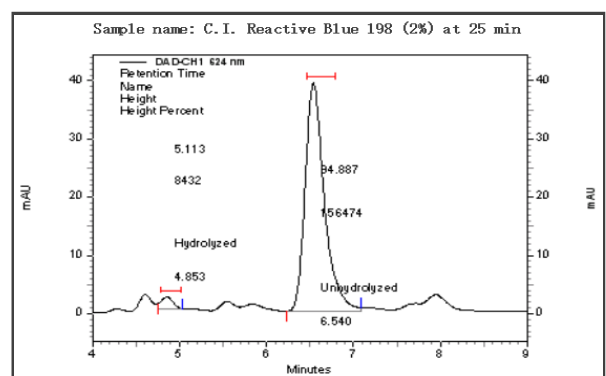

$y = -0.012x + 5.057$
$R^2 = 0.969$

Figure -3.6: Relation between log Ct and time of after addition of alkali to the dye bath for C. I. Reactive Blue 198 (1%)

(C)

(D)

(E)

(F)

(G)

(H)

(I)
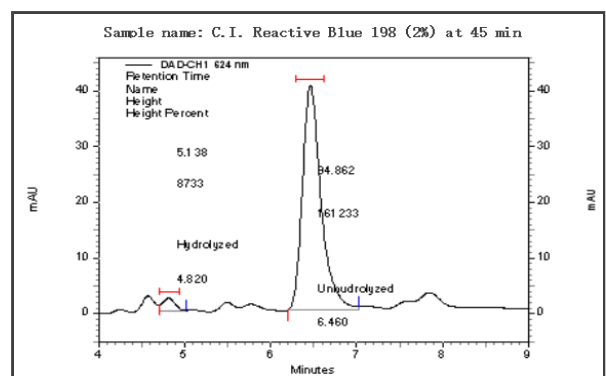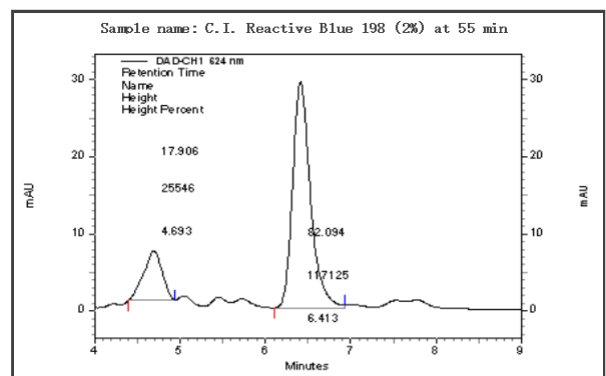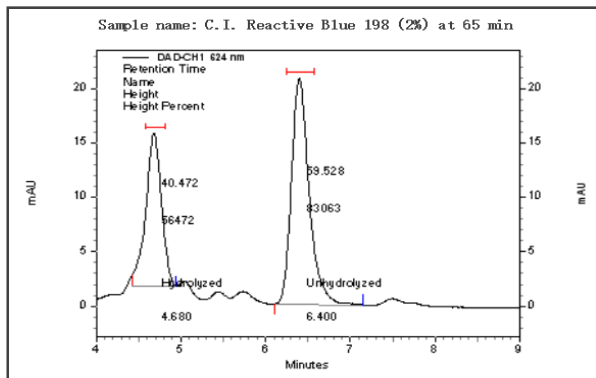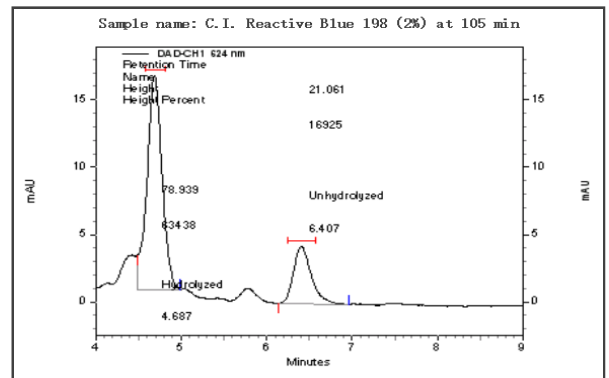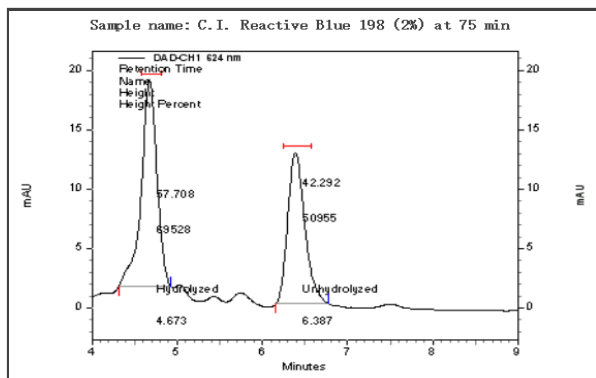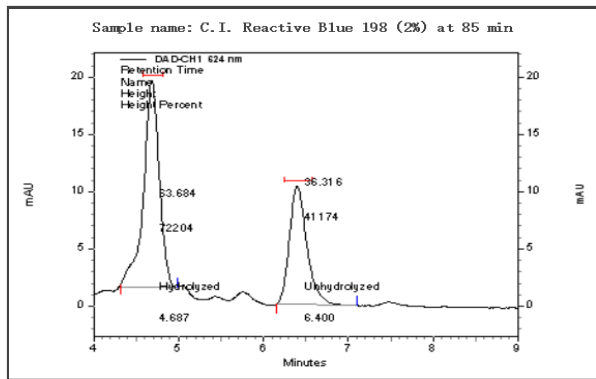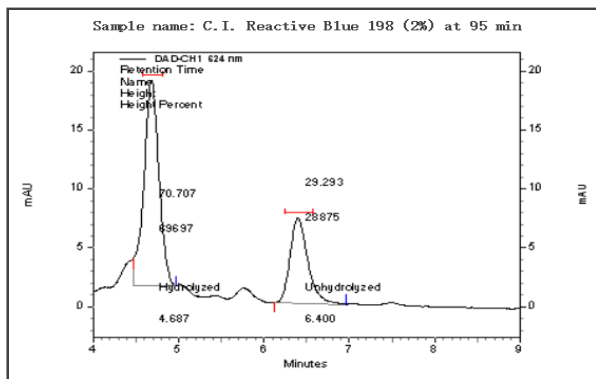
Figure -3.7: HPLC Result of C.I. Reactive Blue 198 dyes 2% (A) 0 min (B) 25min (C) 45min (D) 55min (E) 65min (F) 75min (G) 85min (H) 95min (I) 105min.

Table -3.3: Extent of hydrolysis of C.I. Reactive Blue 198 2% at different time

Time, min	Unhydrolyzed dye, %	Hydrolyzed dye, %	log Ct	Rate constant, min^{-1}
0	95.18	4.82	4.56	
25	94.89	5.11	4.55	
45	94.86	5.14	4.55	
55	82.09	17.91	4.41	
65	59.53	40.47	4.09	0.025
75	42.29	57.71	3.74	
85	36.32	63.68	3.59	
95	29.29	70.71	3.38	
105	21.06	78.94	3.05	

Figure -3.8: Relation between amount of hydrolyzed dye and time of treatment for C. I. Reactive Blue 198 (2%)

Figure -3.9: Relation between log Ct and time of t after addition of alkali to the dye bath for C. I. Reactive Blue 198 (2%)

The graph of hydrolyzed against time Figure (3.2, 3.5, 3.8), indicates that there was no hydrolysis shown between 0 to 45 min and after addition of alkali at 45 min hydrolysis of dyes began and it increased with the increase in time and the maximum hydrolysis was reached at at 105 min.
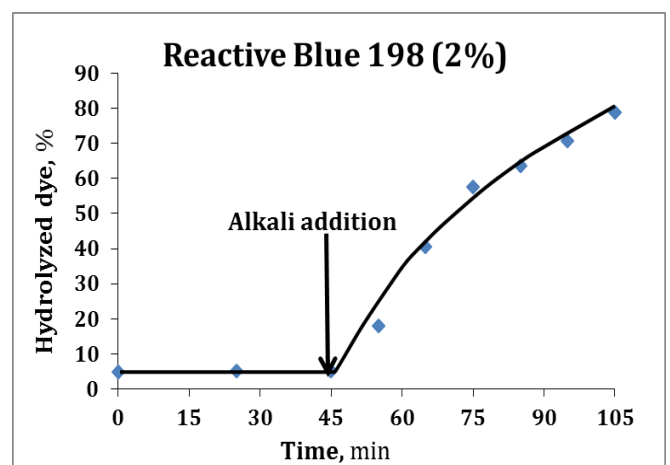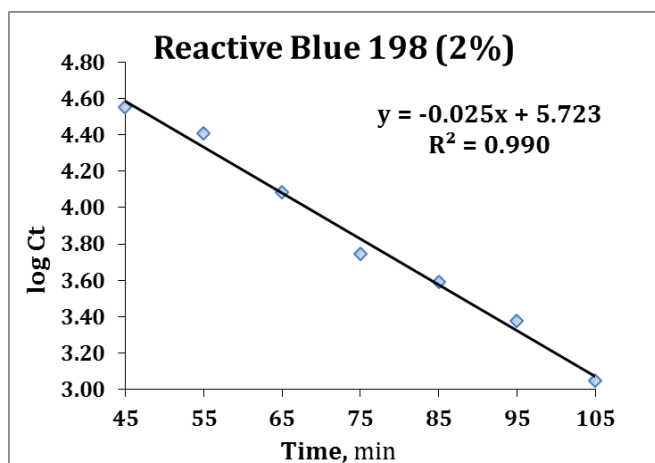
As hydrolysis occurred after 45 min at alkaline pH, so rate constant of hydrolysis was determined from 45 to 105 min Figure (3.3, 3.6, 3.9). From the Figure (3.3, 3.6, 3.9) the rate constant are 0.011 min^{-1}, 0.012 min^{-1} and 0.025 min^{-1} which indicate the rate of hydrolysis of 2% dye concentration was more than 1% and then 0.5%.

From all above result it was shown that as the concentration of dyes increases the rate of hydrolysis increases because of more number of molecules of dyes as well as more number of Na_2CO_3 were available in the dye bath, and -OH group found more number of dyes for reacting.

4. CONCLUSIONS

The kinetic of the hydrolysis of a bi-functional reactive dye in neutral and alkaline pH have been studied by utilizing HPLC technique and rate constants of hydrolyzed dye measured.

The kinetic study of the hydrolysis of reactive dyes help in optimizing the dwell time expected for dyeing of textile fibre/yarn/fabric in the presence of alkali. Thus, it saved from more hydrolysis of reactive dyes, the hydrolyzed dye has no bonding toward cellulose fiber, during washing-off it gets removed and affects the environment.

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BIOGRAPHIES

Mr. Anjum Ahmad, completed his M. Tech. in Fibres and Textile Processing Technology at Institute of Chemical Technology, Mumbai. His research area include works on Kinetic study of hydrolysis of reactive dye by HPLC, Eco friendly reactive dyeing.

Prof. Ashok Athalye, is a fellow Society of dyes and Colourist (SDC-UK), over 25 years of experience in technical services of textile colorants & process chemicals, travelled widely for technical interaction, Published over 73 research & review articles in technical journals

Prof. Sanjeev R. Shukla, is a Fellow of Maharashtra Academy of Sciences, Member Editorial Board Indian Journal of Fibres & Textile Research, Life Member of Indian Fibre Society, Life Member of Textile Association (India), Life Member of Colour Group of India, has guided over 105 Master's and Doctoral students with over 310 publications/ conference presentations.