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Environment Friendly Approach to Simultaneously Remove Unfixed Dyes from Textile Fabric and Wash-off Liquor

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Abstract
A new idea was investigated in this study wherein the use of coagulants was assessed in the wash-off process to simultaneously remove unfixed reactive dyes from fabrics and wash-off liquor. At the end of dark shade dyeing (5% owf) with C.I. Reactive Yellow 145, C.I. Reactive Red 194, and C.I. Reactive Black 5, fabrics were subjected to both conventional and new wash-off methods, and comparisons were made. The effectiveness of coagulant wash-off was evaluated in terms of the change in shade, wash fastness, rubbing properties, and colour difference values (ΔL,ΔC*, Δh* & ΔE*). The colour removal efficiency (%) of liquor was considered as indicative of the removal of unfixed dyes from the fabric. Overall results have shown that the use of alum and $MgCl_2$ coagulants during the wash-off process can achieve up to an 87% reduction in the colour of wash-off liquor, without compromising the colour properties of the dyed substrate.*

Key words: *coagulants, wash-off, reactive dyes, unfixed dyes, colourfastness.*

Introduction

Stringent international laws and increased public concern about the environment have challenged the industries to develop eco-friendly processes [1]. In textile dyeing and finishing units, water is extensively used in almost every step of different processes [2]. One of the most expensive, time-consuming and polluting processes in textile colouration is the removal of loosely bound unfixed or hydrolyzed dyes from a textile substrate [3]. The wash-off process consumes large quantities of water and produces large volumes of wastewater containing residues of dyes, high temperature, turbidity, and COD & BOD concentration [4]. The direct discharge of such wastewater into water bodies without adequate treatment contaminates the water and adversely affects many species of aquatic flora and fauna [5, 6].

The wash-off step to remove unfixed dyes is critical to guarantee acceptable colour fastness properties in the final dyed material [7]. When reactive dyes are applied in deep shades, difficulties are encountered in removing the unfixed dyes. Numerous studies have been conducted in the past to optimise the wash-off process by using a variety of chemicals including enzymes, surfactants, cationic fixing agents, aqueous alkalis, and anionic and non-ionic detergents [8 - 12]. The removal of unfixed dyes from fabric using ozone (O_3) and ultrasonic energy during the wash-off process has been investigated by some researchers [13, 14]. Attempts were also made to design and synthesise easy wash-off reactive dyes [15].

This study evaluates the use of selected coagulants in the wash-off process of reactive dyeing to achieve simultaneous removal of unfixed reactive dyes from dyed fabric and wash-off liquor. The removal of colour from dye-containing effluents by coagulation is most common, and widely practiced both in developed and developing countries due to its low capital cost [16 - 18]. It seems that most of the relevant studies of coagulation have been focused only on the decolourisation of textile effluents [19 - 23]. To the best of our knowledge, no studies related to the use of coagulant as a wash-off agent for reactive dyes have been published in the research or patent literature.

Materials and methods

The textile substrate used in this study consisted of 100% cotton single jersey knitted fabric of 200 g/m^2 surface weight. The fabric had already been bleached (ready for dyeing) with hydrogen peroxide in an industrial process, and was provided by Sapphire Fibres, Pakistan. Samples of reactive dyes were kindly supplied by DyStar, Pakistan. The main characteristics and chemical structures of the dyes are shown in ***Table 1*** and ***Figure 1***, respectively. All the other chemicals used, including sodium sulfate (Na_2SO_4) and sodium carbonate (Na_2CO_3), alum ($Al_2(SO_4)_3$), and magnesium chloride ($MgCl_2$), were of commercial grade and used without any further purification.

Dyeing procedure

Deep shade dyeing (5% owf) of CI Reactive Yellow 145, C.I. Reactive Black 5, and C.I. Reactive Red 194 was carried out individually on 10-g samples consisting of two fabric swatches, each weighing 5 grams. Dyeing took place on a Datacolor Ahiba Nuance (New Jersey, USA) laboratory-scaled dyeing machine at a liquor ratio (L:R) of 1:10 using an

Table 1. *Characteristics of dyes used in the study.*

Chemical name	Commercial name	Maximum absorption (λ_{max}), nm	Functional group
C.I. Reactive Yellow 145	Synozol Golden Yellow HF-2GR 150%	419	bifunctional, sulphatoethylsulphone (SES) and monochlorotriazine (MCT)
C.I. Reactive Black 5	Remazol Black B 150%	597	sulphatoethylsulphone (SES)
C.I. Reactive Red 194	Synozol Red HF-3B	523	bifunctional, sulphatoethylsulphone (SES) and monochlorotriazine (MCT)

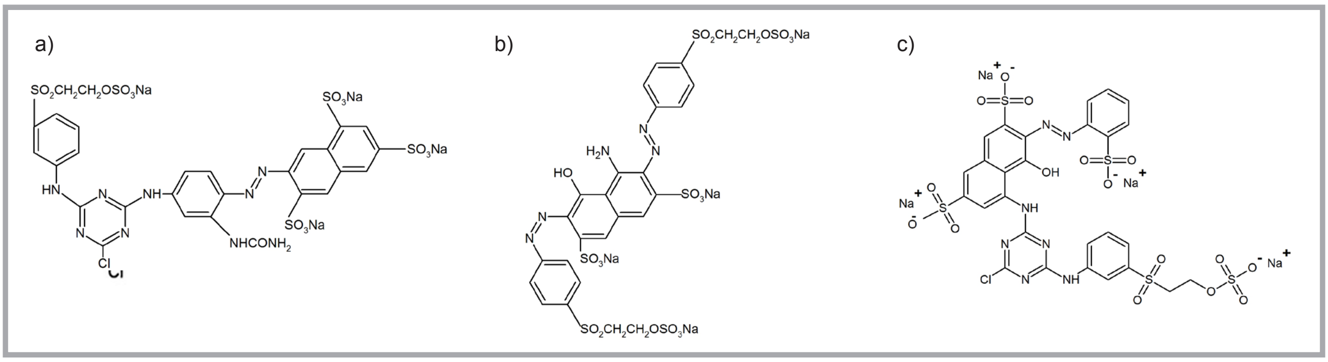

Figure 1. Chemical structures of dyes used in the study: a) C.I. Reactive Yellow 145, b) C.I. Reactive Black 5, c) C.I. Reactive Red 194.

isothermal all-in-one dyeing method as shown in ***Figure 2***.

Wash-off procedure

At the completion of the dyeing process, one 5-garm fabric swatch was given conventional wash-off treatment as shown in ***Table 2***, and regarded as a reference sample. The remaining 5-gram fabric sample was subjected to a new wash-off method containing coagulants, alum ($Al_2(SO4)_3$) and magnesium chloride ($MgCl_2$), and the sample treated was compared with the reference one. The coagulants were added directly in all wash-off steps the same way as detergents in the conventional wash-off. The spent wash-off baths from both methods were also saved, and a comparison was made in terms of the colour strength of the liquor.

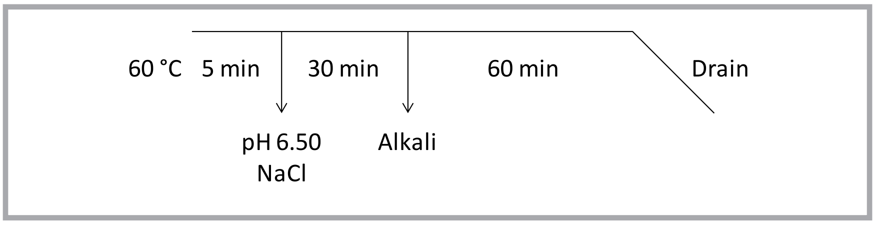

***Figure 2**. Dyeing procedure.*

***Table 2.** Conventional wash-off steps.*

Step	Operation	Temp, °C	Time, min	Water consumption, ml (L:R = 1:10)
1	Cold rinse	30	10	80
2	Neutralisation with acetic acid	30		
3	Warm Wash	50		
4	Hot wash	80		
5	Warm wash	50		
6	Cold wash	30		

Colour measurements

The reference and coagulant treated fabric samples were subjected to reflectance measurements using a spectrophotometer Spectraflash 600 PLUS-CT (Datacolor, USA) under illuminant D65, using a 10° standard observer with the specular component excluded and UV component included. Each fabric was folded to achieve four thicknesses and an average of four readings was taken. The colour strength of the dyed samples was presented in terms of the K/S value calculated by the Kubelka–Munk equation.

Colour fastness testing

Fastness properties to rubbing (wet and dry) and washing of the dyed samples were evaluated according to ISO 105-X12 (2001) and ISO 105-C06/A2S (2006), respectively.

Measurement of colour removal

Wastewater from both conventional and coagulant wash-off was measured at a wavelength corresponding to their maximum absorption (λ_{max}) using a UV-visible spectrophotometer DR/4000 (HACH, USA). The decolourisation efficiency was determined based on the absorbance changes using ***Equation 1***:

$$\text{Colour removal} = (A_0 - A)/A_0 \times 100 \text{ in \%} \quad (1)$$

where, A_0 = absorbance of liquor from conventional wash-off, A = absorbance of liquor from coagulant wash-off.

Results and discussion

Effect of pH on coagulation performance

The initial pH of effluent is an important parameter in the coagulation process because every coagulant displays a maximum colour removal at its optimum pH [24]. In order to determine the optimum pH values of Alum and $MgCl_2$ for the removal of colour from wash-off liquors, a constant dose of coagulant (500 ppm) was added at different pH values, adjusted using acetic acid or NaOH solutions. The effects of the initial pH on the colour removal efficiency of Alum and $MgCl_2$ are shown in ***Tables 3*** and ***4*** (see page 126), respectively. The results clearly indicate that the optimum pH ranges for alum and $MgCl_2$ treatments are 4.0 - 5.0 and 11.0 - 12.0, respectively. Alum performed well near pH 5, where colour removal efficiency was found up to 90%. In the case of $MgCl_2$, the wash-off liquors underwent maximum decolourisation (96%) at a higher pH range. These results are in agreement with the findings of other researchers [25, 26].

Effect of coagulant dose

Determination of an appropriate dose of coagulant is considered as one of the most important parameters for their performance in the colour removal process. An insufficient dosage or overdosing would result in poor performance. Moreover an optimum dosage of coagulant also minimises the dosing cost and sludge formation [27]. The effect of coagulant doses (100 – 500 ppm) on the removal of colour from different wash-off liquors using alum (pH 5) and $MgCl_2$

Table 3. Effect of pH on colour removal efficiency of Alum for various wash-off steps.

Dyes	pH	Colour removal, %						
		Cold wash (30 °C)	Neutralisation (30 °C)	Warm wash (50 °C)	Hot wash (80 °C)	Warm wash (50 °C)	Cold wash (30 °C)	Combined wash liquor
C.I. Reactive Yellow 145	5	85	60	80	30	88	90	78
	6	79	34	71	28	72	43	66
	7	76	37	70	18	76	40	59
C.I. Reactive Red 194	5	79	58	81	39	81	76	81
	6	70	44	67	37	63	55	70
	7	67	33	45	22	56	38	55
C.I. Reactive Black 5	5	68	59	71	29	83	66	68
	6	43	24	37	17	26	16	41
	7	37	25	25	9	14	71	42

Table 4. Effect of pH on colour removal efficiency of $MgCl_2$ for various wash-off steps.

Dyes	pH	Colour removal, %						
		Cold wash (30 °C)	Neutralisation (30 °C)	Warm wash (50 °C)	Hot wash (80 °C)	Warm wash (50 °C)	Cold wash (30 °C)	Combined wash liquor
C.I. Reactive Yellow 145	10	28	13	4	2	3	7	4
	11	46	47	94	6	53	30	48
	12	84	53	95	18	72	37	78
C.I. Reactive Red 194	5	35	25	17	16	9	5	25
	6	39	37	55	25	47	25	48
	7	77	60	88	79	86	88	80
C.I. Reactive Black 5	10	62	2	25	12	35	23	12
	11	78	55	74	33	35	26	67
	12	87	96	95	37	92	91	87

Table 5. Effect of dosage on the colour removal efficiency of Alum for various wash-off steps.

Dyes	Alum dosage, ppm	Colour removal, %						
		Cold wash (30 °C)	Neutralisation (30 °C)	Warm wash (50 °C)	Hot wash (80 °C)	Warm wash (50 °C)	Cold wash (30 °C)	Combined wash liquor
C.I. Reactive Yellow 145	100	12	50	39	60	32	23	45
	200	42	39	35	66	66	33	39
	300	71	68	48	81	72	38	58
	400	85	60	71	62	74	62	72
	500	85	48	74	56	87	83	79
C.I. Reactive Red 194	100	38	23	44	32	23	41	40
	200	46	44	59	46	33	49	51
	300	65	69	74	62	51	65	65
	400	77	72	84	74	69	81	81
	500	84	69	87	79	74	84	86
C.I. Reactive Black 5	100	47	23	27	13	57	20	31
	200	53	24	48	36	53	52	63
	300	68	52	71	29	83	83	68
	400	59	57	66	63	88	83	70
	500	54	42	46	72	16	16	58

(pH 11) are presented in ***Tables 5*** and ***6***, respectively. Overall results suggest that the colour removal efficiency increases as the dose of coagulant increases. In the case of alum, a dose of 100 and 500 ppm yielded 23 to 60% and 48 to 87% colour removal, respectively, from various wash-off liquors containing CI Reactive Yellow 145 dye. At 500 ppm of alum concentration, the colour of combined wash-off liquor (addition of individual washes) from the dyeing of CI Reactive Yellow 145 was found to be 79% less coloured as compared to that of the conventional wash-off process. For CI Reactive Red 194 and CI Reactive Black 5, alum doses of 500 and 400 ppm achieved 86 and 70% colour removal, respectively. The use of $MgCl_2$ for the removal of CI Reactive Yellow 145, CI Reactive Red 194 and CI Reactive Black 5 from combined wash-off liquor exhibited 78, 82, and 87% colour removal, respectively. The optimum dose of $MgCl_2$ was found to be 400 ppm for all three dyes.

Effect on colour properties

CIELAB colour differences between the reference fabric and those washed-off with alum and $MgCl_2$, are summarised in ***Tables 7*** and ***8***, respectively. Overall results indicate that there is a steep change in shade with increasing coagulant concentration. The shade of coagulant treated fabrics became darker ($-\Delta L^*$) and duller ($-\Delta C^*$) when the coagulant concentration was gradually increased. The results of C.I. Reactive Yellow 145 dyed fabric show that treatment of 100 ppm of alum exhibited negligible dif-

Table 6. Effect of dosage on the colour removal efficiency of $MgCl_2$ for various wash-off steps.

Dyes	$MgCl_2$ dose, ppm	Colour removal, %						
		Cold wash (30 °C)	Neutralisation (30 °C)	Warm wash (50 °C)	Hot wash (80 °C)	Warm wash (50 °C)	Cold wash (30 °C)	Combined wash liquor
C.I. Reactive Yellow 145	100	17	85	80	3	9	50	37
	200	31	86	85	7	16	66	42
	300	84	53	86	5	32	40	74
	400	94	90	95	16	72	50	78
	500	88	75	84	1	8	30	63
C.I. Reactive Red 194	100	41	43	75	12	23	47	44
	200	49	67	86	26	53	51	58
	300	78	75	91	33	59	77	75
	400	89	80	95	41	74	81	82
	500	89	76	96	43	50	47	68
C.I. Reactive Black 5	100	32	28	71	2	50	25	35
	200	83	84	91	2	50	42	75
	300	90	98	98	21	71	85	81
	400	87	96	95	37	92	91	87
	500	94	92	91	2	65	33	82

ferences in lightness (ΔL^* = 0.30), hue (ΔC^* = -0.56), and the total colour difference ($\Delta E_{cmc(2:1)}$ = 0.32). Similarly the total colour difference ($\Delta E_{cmc(2:1)}$ = 0.71) between the reference and 200ppm alum treated sample confirm that colour properties of the treated fabric were comparable to those of the reference sample. When the concentration of alum was increased to 500ppm, the shade of the sample was found to be darker (ΔL^* = -0.87), greener (Δa^* = -0.87), duller (ΔC^* = -0.93) and yellower (Δb^* = 0.31), with the total colour difference being perceivable ($\Delta E_{cmc(2:1)}$ = 1.73). In the case of CI Reactive Red 194, an acceptable colour difference ($\Delta E_{cmc(2:1)} \leq 1.0$) was achieved when the alum dose was ranged between 100 to 300 ppm. Fabric samples dyed with CI Reactive Black 5 showed the lowest and highest colour differences of $\Delta E_{cmc(2:1)}$ = 0.56 and $\Delta E_{cmc(2:1)}$ = 1.67 at alum doses of 100 and 400 ppm, respectively.

Fabric samples washed-off with $MgCl_2$ followed the same pattern as the alum treated samples-$\Delta E_{cmc(2:1)}$ values increased with the increasing concentration of coagulant. The colour strength (K/S) values of all dyed samples confirmed the fact that the depths of shade became darker when the amount of coagulant was gradually increased in the wash-off process.

Colour fastness properties

A comparison of fastness properties (crock fastness and staining ratings) of the reference and coagulant-treated dyed samples is reported in ***Table 9*** (see page 128). Overall results show that both the reference and coagulant-treated samples exhibited similar rubbing and wash fastness properties mostly in the range of 4/5 to 5.0. The fabric sample dyed with CI Reactive Yellow 145 and washed-off with alum at 100 ppm concentration showed 4/5 wet rubbing, which was half a point less than that of

Table 7. CIELab colour differences of Alum treated fabrics and reference.

Dyes	Alum dosage, ppm	Colour difference values					
		ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE*
CI Reactive Yellow145	100	0.30	0.10	0.69	0.56	0.70	0.65
	200	0.34	0.38	0.89	0.97	0.01	0.71
	300	-1.55	0.17	0.26	0.31	-0.05	0.79
	400	-0.98	0.18	0.25	0.30	-0.07	0.88
	500	-1.93	-0.87	1.03	-0.93	2.15	1.73
CI Reactive Red 194	100	0.24	0.18	0.79	0.77	0.25	0.41
	200	-0.27	0.20	0.39	0.65	-0.47	0.56
	300	-0.67	0.80	-0.67	-0.89	0.50	0.78
	400	-1.44	0.57	-1.33	-1.19	0.60	1.53
	500	-2.12	0.88	-1.5	-1.43	1.19	2.89
CI Reactive Black 5	100	-0.30	0.49	0.76	-0.88	0.411	0.56
	200	-0.94	0.63	0.95	-1.05	0.44	1.06
	300	-1.26	0.80	1.04	-1.17	0.60	1.40
	400	-1.87	-0.08	-0.18	0.19	-0.04	1.67
	500	-1.11	0.25	0.11	-0.16	0.23	1.35

Table 8. CIELab colour differences of $MgCl_2$ washed-off fabrics and reference.

Dyes	$MgCl_2$ dose, ppm	Colour difference values					
		ΔL*	Δa*	Δb*	ΔC*	ΔH*	ΔE*
CI Reactive Yellow145	100	0.82	-1.69	-1.59	-2.13	0.92	0.99
	200	0.71	-1.59	-1.70	-2.20	0.78	0.65
	300	1.10	-0.78	-0.16	-0.45	0.66	1.44
	400	2.31	-1.18	-1.56	-2.29	1.39	1.54
	500	1.35	-1.57	0.35	0.10	0.66	1.84
CI Reactive Red 194	100	0.61	1.39	-1.61	-1.90	0.87	0.79
	200	0.63	0.71	-1.11	-1.19	1.12	0.96
	300	-0.98	0.49	-0.17	0.51	-0.02	1.17
	400	-1.15	0.72	-0.35	-0.90	-0.66	1.42
	500	-1.71	0.18	-1.36	-2.17	1.39	2.54
CI Reactive Black 5	100	-0.97	0.35	0.46	-0.52	0.26	0.88
	200	-1.36	0.61	0.34	-0.45	0.54	1.36
	300	-1.55	-0.61	-1.88	2.95	-0.01	1.75
	400	-1.50	0.52	-1.07	1.15	0.87	2.11
	500	-1.66	1.01	0.24	-0.41	0.96	2.33

***Table 9**. Colour fastness and change in shade properties of dyed fabrics.*

Dyes	Wash-off method		Rubbing		Staining			Colour change
	Coagulant	Dosage, ppm	Dry	Wet	Cotton	Nylon	Polyester	
CI Reactive Yellow 145	Reference		5	5	4-5	5	5	-
	Alum	100	5	4-5	4-5	5	5	5
		200	5	4-5	4-5	5	5	4-5
		300	5	5	5	5	5	4-5
		400	5	5	5	5	5	4-5
		500	5	5	5	5	5	4
	$MgCl_2$	100	5	4-5	4-5	5	5	4-5
		200	5	4-5	4-5	5	5	4-5
		300	5	5	5	5	5	4-5
		400	5	5	5	5	5	4
		500	5	5	5	5	5	4
CI Reactive Red 194	Reference		5	4-5	4-5	5	5	-
	Alum	100	5	4-5	4	4-5	5	5
		200	5	4-5	4	5	5	4-5
		300	5	4-5	4	5	5	4-5
		400	5	4-5	4	5	5	4
		500	5	4-5	4	5	5	4
	$MgCl_2$	100	5	4-5	4-5	5	5	4-5
		200	5	4-5	4-5	5	5	4-5
		300	5	5	4-5	5	5	4-5
		400	5	5	4-5	5	5	4
		500	5	5	4-5	5	5	4
CI Reactive Black 5	Reference		5	5	5	5	5	-
	Alum	100	5	5	4-5	5	5	4-5
		200	5	5	4-5	5	5	4-5
		300	5	5	5	5	5	4-5
		400	5	5	5	5	5	4-5
		500	5	5	5	5	5	4
	$MgCl_2$	100	5	4-5	4-5	5	5	5
		200	5	5	5	5	5	4-5
		300	5	5	5	5	5	4-5
		400	5	5	5	5	5	4
		500	5	5	5	5	5	4

the reference fabric; however, at this concentration, no change of shade (5 rating) observed. When the alum concentration was increased to 200ppm, all fastness parameters became identical to those of the reference. At an alum concentration between 300 and 500 ppm, staining to cotton was found to be half a point better compared to that of the reference. The results obtained suggest that an alum concentration of 200 - 300 ppm is good enough to yield acceptable fastness properties. The other two dyeings with CI Reactive Red 194 and CI Reactive Black 5 showed almost identical fastness properties on both the reference and coagulant-treated dyed samples when the alum dose was adjusted to 200 ppm. A similar trend was noticed when all three dyeings were washed-off with $MgCl_2$. A significant change in shade was noticed in samples washed-off with higher concentrations of coagulants (300 - 500 ppm). These results could be attributed to possible changes in the hue of dyed material imparted with a high dose of coagulants in the wash-off.

Summary and conclusions

This research evaluated a new wash-off method for simultaneously removing surface-deposited unfixed dyes from cotton fabric and liquor used in the wash-off process. Unfixed dyes were removed by controlled addition of coagulants, either alum or $MgCl_2$, to attain the level of colour fastness required. The efficiency of the new method was investigated for cotton fabrics dyed with C.I. Reactive Yellow 145, C.I. Reactive Red 194, and C.I. Reactive Black 5 in deep shades (5% owf). Based on the results obtained in this study, the coagulant-based wash-off method can produce similar colour fastness properties with an acceptable colour difference at a lower dose (100 - 200 ppm) of coagulants. The higher dose (300 - 500 ppm) of coagulants yielded improved fastness properties accompanied by an increased total colour difference (ΔE^*) and change of shade. Moreover the new wash-off method can significantly reduce (up to 87%) colour in wastewater that is generated during the wash-off process. It is recommended that the effect of coagulants on different substrates dyed with various classes of reactive dyes should be investigated in pilot-scale studies to evaluate the suitability of the method for commercial applications.

References

1. Li Q, Hurren CJ, Ding C, Wang L, Lin T, Wang X. Ultrasonic scouring of wool and its effects on fibre breakage during carding. *Journal of The Textile Institute* 2011; 102: 1059–1064.
2. Żyłła R, Sójka-Ledakowicz J, Michalska K, Kos L, Ledakowicz S. Effect of UV/H2O2 on Fouling in Textile Wastewater Nanofiltration. *Fibres & Textiles in Eastern Europe* 2012: 20 (1): 99-104.
3. Koh J. Alkali-hydoylsis kinetics of alkali-clearable azo disperse dyes containing a fluorosulphonyl group and their fastness properties on pet/cotton blends. *Dyes and Pigments* 2005; 64: 17–23.
4. Burkinshaw SM, Kabamb O. Attempts to reduce water and chemical usage in the removal of reactive dyes: Part 1 bis(aminochlorotriazine) dyes. *Dyes and Pigments* 2009; 83: 363-374.
5. Blanchard E J. Dye ability of cross linked cationic cotton fabrics. *Textile Chemist & Colourist* 1988; 20: 25-29.
6. Moussa A, Ghali AE, Ellouzi S, Sakli F. Colour and fastness study of wool dyeing in multiple reuse dye baths using acid and reactive dyestuffs in laboratory scale. *The Journal of the Textile Institute* 2013; 104: 260–269.
7. Mughal JM, Naeem M, Aleem A, Saeed R, Ahmed K. Effect of a cationising agent on the conventional reactive dyeing of cotton. *Coloration Technology* 2008; 124: 62-65.
8. Haas J, Koenemund B, Vogt U. New and better way to wash-off reactive dyestuffs. *Melliand International* 2000; *6:* 243-244.
9. Dvarioniene J, Stasiskiene Z, Knudsen HH. Pilot-scale membrane filtration study on water eeuse of rinsing water after reactive cotton dyeing. *Environmental Research Engineering and Management* 2005; 3: 3-10.
10. Burkinshaw SM, Katsarelias D. A study of the wash-off and aftertreatment of dichlorotriazinyl reactive dyes on cotton. *Dyes and Pigments* 1995; 29: 139-153.
11. Burkinshaw SM, Katsarelias D. The wash-off of reactive dyes on cellulosic fibres. Part 4: The use of different alkalis with monochlorotriazinyl dyes on cotton. *Dyes and Pigments* 1997; 35: 249-259.
12. Akcakoca EP, Ozguney AT, Atav R. The efficiency of washing agents in the post-dyeing removal of hydrolyzed reactive dye. *Dyes and Pigments* 2007; 72: 23-27.

13. Shaikh IA, Ahmad N, Urooj F. A novel method to improve color fastness of deep shade reactive dyeing using ozone in washing off. *AATCC Review* 2010; 10: 73–77.
14. Akalin M, Merdan N, Kocak D. Effects of ultrasonic energy on the wash fastness of reactive dyes. *Ultrasonics* 2004; 42:161–164.
15. Suwanruji P, Freeman HS. Design, synthesis and application of easy wash-off reactive dyes. *Coloration Technology* 2006; 122: 27–36.
16. Verma AK, Dash RR, Bhunia P. A review on chemical coagulation/flocculation technologies for removal of colour from textile wastewaters. *Journal of Environmental Management* 2012; 93: 154-168.
17. Anjaneyulu Y, Chary NS, Raj DSS. Decolourization of industrial effluentsavailable methods and emerging technologies-A Review. *Reviews in Environmental Science and Biotechnology* 2005; 4: 245-273.
18. Golob V, Vinder A, Simonic M. Efficiency of coagulation/flocculation method for treatment of dye bath effluents. *Dyes and Pigments* 2005; 67: 93-97.
19. Papic S, Koprivanac N, Bozic AL. Removal of reactive dyes from wastewater using Fe(III) coagulant. *Coloration Technology* 2000; 161: 352–358.
20. Kim TH, Park C, Shin EB, Kim S. Decolourization of disperse and reactive dyes by continuous electrocoagulation process. *Desalination* 2002; 150: 165–175.
21. Georgiou D, Aivazidis A, Hatiras J, Gimouhopoulos K. Treatment of cotton textile wastewater using lime and ferrous sulfate. *Water Research* 2003; 37: 2248–2250.
22. Errais E, Duplay J, Darragi F. Textile dye removal by natural clay – Case study of Fouchana Tunisian clay. *Environmental Technology* 2010: 31: 373-38.
23. Wong PW, Teng TT, Rahman NA, Norulaini N. Efficiency of the Coagulation-Flocculation method for the treatment of dye mixtures containing disperse and reactive dye. *Water Quality Research Journal of Canada* 2007; 42:13-20.
24. Duan J, Gregory J. Coagulation by hydrolyzing metal salts. *Advances in Colloid and Interface Science* 2003; 100: 475–502.
25. Tan BJ, Teng TT, Omar AK. Removal of dyes and industrial dye wastes by magnesium chloride. *Water Research* 2000; 34: 597-601.
26. Ooi PY, Teng TT, Omar AKM, Norulaini NAR. Removal of dyes by aqueous mixed coagulants. *ASEAN Journal of Chemical Engineering* 2005; 5: 52-64.
27. Canizares P, Jiménez C, Martinez F, Rodrigo MA, Sáez C. The pH as a key parameter in the choice between coagulation and electrocoagulation for the treatment of wastewaters. *Journal of Hazardous Materials* 2009; 163: 158–164.

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