A new approach for the removal of unfixed dyes from reactive dyed cotton by Fenton oxidation

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ABSTRACT

The use of fresh water in the textile wash-off process is becoming more expensive day by day due to declining water levels in the region. In this study, the potential of using Fenton oxidation in wash-off cotton reactive dyeing was investigated. The spent wash-off wastewater from one dyeing was first treated with Fenton oxidation, and then reused in several washing-offs employing widely used reactive dyes, C.I. Reactive Yellow 145, C.I. Reactive Blue 21, and C.I. Reactive Red 195. Experimental results showed that at acidic pH (3) using optimized quantities of $FeSO_4$ and H_2O_2, Fenton process yielded a significant reduction (90–95%) of color in 30 minutes of treatment time. New washing-offs were then carried out in Fenton decolorized wash-off wastewater, and dyed cotton fabric samples were subjected to quality evaluations in terms of color difference properties (ΔL*, Δc*,Δb*, Δa*, ΔE*cmc) and wash fastness properties. This study concluded that after Fenton oxidation, treated liquor can be effectively reused subsequent washing-offs without compromising fabric quality parameters as ΔE*cmc was less than 1, and washing and crocking was also in the range of 4.5–5 which is commercially acceptable. Moreover, the difference in color strength in terms of k/s was also negligible.

Key words | color fastness, dyeing, effluent, Fenton oxidation, wash-off

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INTRODUCTION

Water is the basic need of every living organism and one of the most valuable resources on Earth. It covers about two-thirds of the Earth's surface (Akali *et al.* 2011). However, due to the growing population, industrialization and urbanization, the usage of water is increasing, making it more and more scarce and expensive. Many industries, such as textile, paper and pulp, dyeing and printing industries, are causing water pollution by discharging their effluent into water bodies (Christensen *et al.* 2009). The textile industry is one of the major industrial sectors which consumes high volumes of water for its various processes and consequently discharges large amounts of highly polluted water (Patel & Shah 2013). It is estimated that approximately 100,000 different synthetic dyes are produced annually (Tunc *et al.* 2012). Various industries release dyes into wastewater, thus creating environmental issues due to the persistent and recalcitrant nature of dyes (McMullan *et al.* 2001). Reactive dyes are highly colored substances having a chromophore group like azo, anthraquinone, etc., and a substituent, e.g. vinylsulfone, chlorotriazine which attach to the fibers by forming a covalent bond during the dyeing process. Reactive

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dyes are used mostly for the coloration of cellulosic fibers such as cotton. In the dyeing process, almost 50–90% reactive dyes adsorbed to fibers by covalent bond and the remainder underwent hydrolysis, i.e. they react with water, so it is required to wash away the non-bonding dye from fiber by using extensive amounts of water (Pierce 1994). The intense color of wastewater generated with a high chemical oxygen demand (COD) necessitates an efficient treatment process before discharge. Effluent treatment and recycling of water are beneficial to the environment as they reduce the pollution discharge and provide treated wastewater for reuse purposes.

Typically, colored wastewater is treated by conventional physical and chemical methods such as sedimentation, active carbon adsorption, chemical coagulation (Rauf *et al.* 2007). However these techniques have some limitations related to additional treatment due to less efficiency, cost and sludge disposal (El Qada *et al.* 2008). Biological treatment by activated sludge can treat biodegradable waste and can reduce COD but is inefficient for treating non-biodegradable organic matter, also complete color removal is not possible with this method (Bes-Piá *et al.* 2002). The major drawbacks of conventional treatments, including inefficiency in pollutant removal, high costs and large footprint, can be overcome by using an attractive method to improve the biodegradability of industrial effluent. Advance oxidation process (AOPs) is a potential alternative which is a chemical oxidation process that generates and use hydroxyl free radicals ($OH^{\cdot}$) as strong oxidant. Its application is able to reduce contamination and degradation of the dyes present in wastewater. Among AOP's, the Fenton process is one of the promising oxidation techniques (Oller *et al.* 2011; Sin *et al.* 2011).

Fenton's process has been successfully applied for the treatment of textile effluent. Fenton's reagent is found to be effective to achieve complete color and partial COD removal from textile wastewater (Gokkuş *et al.* 2014; Sindhi & Mehta 2014). Fenton's reagent is a mixture of H_2O_2 and ferrous ions in acidic medium that generate hydroxyl radicals with oxidation potential of 2.8 V (Ertugay & Acar 2017). The overall reaction is:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^\bullet$$

Fenton's process is a simple and inexpensive process. The chemicals used are readily available and easy to handle (Gogate & Pandit 2004; Sohrabi *et al.* 2017). Fenton's process has the capacity to treat and eliminate textile dyes in a short reaction time (Ertugay & Acar 2017; Shafeeyan *et al.* 2018). In addition to treating textile waste water, Fenton's process has been applied to a variety of effluents such as treatment of 1-amino-8-naphthol-3,6-disulfonic acid manufacturing wastewater (Zhu *et al.* 1996), reduction of polynuclear aromatic hydrocarbons in water (Beltran *et al.* 1998), improvement in dewatering of activated sludge (Lu *et al.* 2003), removal of adsorbable organic halogens (AOX) from pharmaceutical wastewater (Hofl *et al.* 1997), treatment of brines or treatment of paper and pulp manufacturing effluents (Perez *et al.* 2002), and treatment of metal containing industrial effluent (Lou & Huang 2009).

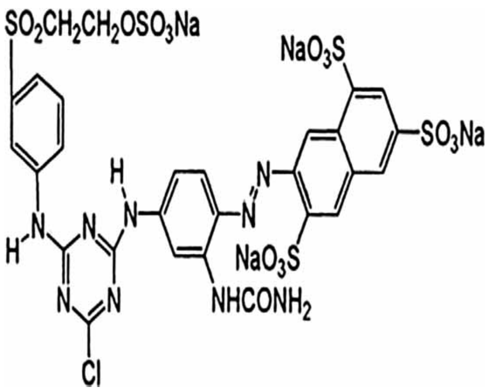
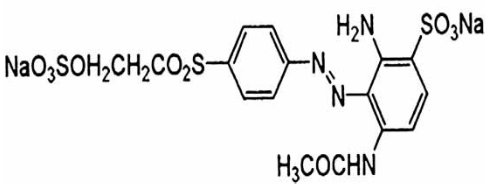
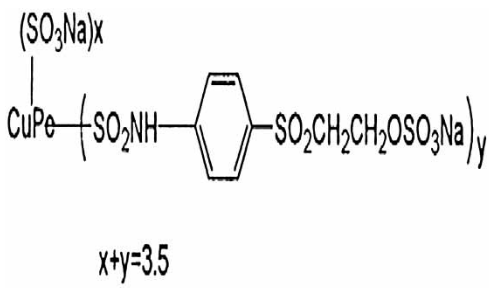
Different studies have suggested that after treatment of wastewater, it can be reused in other industrial processing (Mangat *et al.* 2014; Shaikh *et al.* 2014). Textile wastewater reclamation and reuse can conserve water and help in reducing environmental pollution (Lu *et al.* 2010). It is very common to use clean and expensive water in textile dyeing processes (Erdumlu *et al.* 2012). After dyeing, a wash-off process is employed to remove unfixed hydrolyzed dyes from the fiber to enhance crock fastness and wash fastness properties (Broadbent *et al.* 1998). The wash-off process is the most water consuming step in the dyeing process as it requires several cold (40–60 °C) and hot (80–98 °C) rinses (Burkinshaw & Salihu 2018; Hu *et al.* 2018). The treatment and reuse of wash-off wastewater offers a potential saving in water usage (Mangat *et al.* 2014; Shaikh *et al.* 2014).

In this study, the treatment of wash-off liquor was carried out by Fenton oxidation and treated wastewater was reused in the next dyeing process. The efficiency of the Fenton process for removing the hydrolyzed dyes is compared by evaluating the washed fabrics and washing liquors.

MATERIAL AND METHODS

In this research work, pre-bleached single jersey cotton knitted fabric having a weight of 200 g/m^2 was used. Samples of commercial dyes, C.I. Reactive Yellow 145, C.I. Reactive Blue 21, and C.I. Reactive Red 195 were

Table 1 | Characteristics of dyes used in the study

Dye	Molecular formula	Chemical structure	Molecular weight g/mol	Maximum absorption
C.I. Reactive yellow 145	$C_{28}H_{20}ClN_9Na_4O_{16}S_5$		1,026.26	417 nm
C.I. Reactive Red195	$C_{31}H_{19}ClN_7Na_5O_{19}S_6$		1,136.32	517 nm
C.I. Reactive Blue 21	$C_{40}H_{25}CuN_9O_{14}S_5$		1,079.535	665 nm

kindly provided by KISCO Dyes, Korea. Table 1 shows the chemical structures of these dyes. The chemical auxiliaries such as sodium chloride, sodium carbonate and sodium hydroxide used in the dyeing process were of commercial grade and used without any purification. During the wash-off process, acetic acid was used for neutralization and 1 g/L Dekol SN was used in the soaping step as the soaping-off agent.

Dyeing and wash-off steps

Ten grams of cotton fabric was dyed individually with a 5% shade depth consisting of two fabric swatches (5 g each) with a liquor ratio of 1:10 using 80 g/L of sodium chloride and 20 g/L of sodium carbonate for each synthetic dye stuff. As Figure 1 shows, the dyeing process for each type of dye stuff was accomplished at 60 °C for 60 minutes using an isothermal dyeing method. All dyeing experiments were carried out in sealed 300 mL capacity stainless steel dyeing pots housed in an AHIBA Nuance Laboratory dyeing machine by Datacolor. The dyeing method conditions are schematized in Figure 1. To remove unfixed dyes, fabric was washed-off after dyeing. One 5 g dyed fabric swatch was washed-off according to conventional methods as shown in Table 2, in which fabric was constantly stirred in each step and this fabric was regarded as reference.

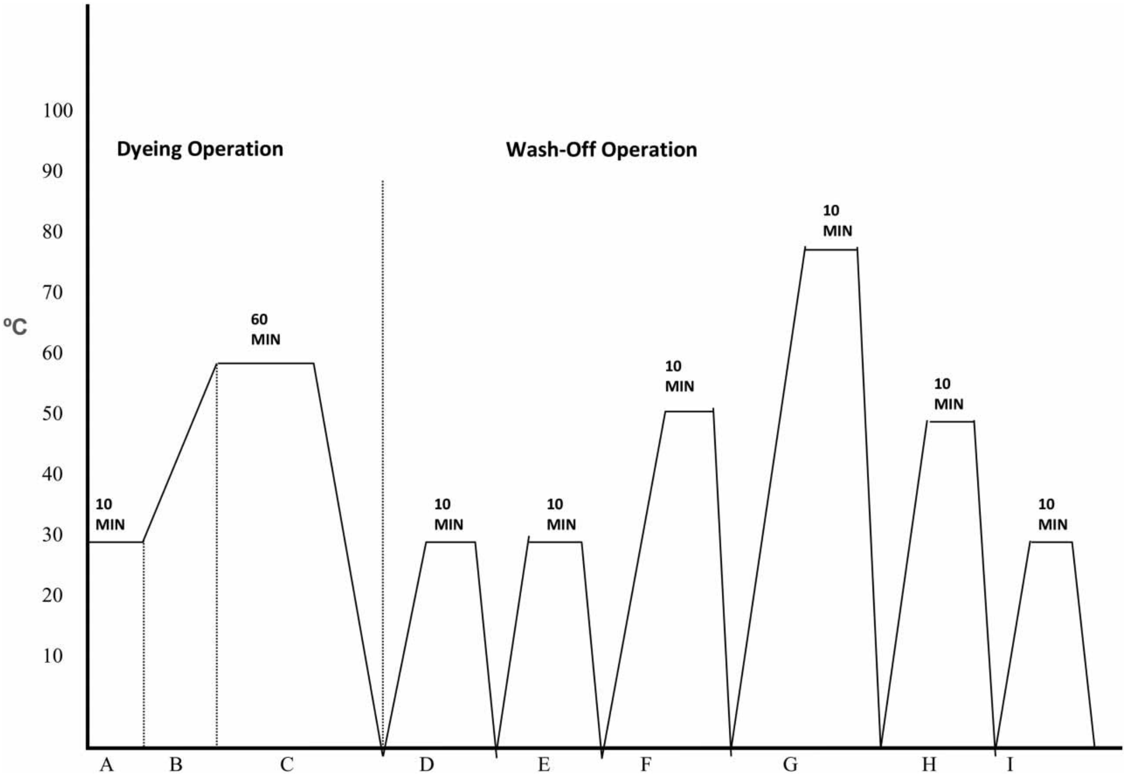


Figure 1 | Isothermal dyeing process. A: Cold dyeing; B: Salt addition; C: Sodium carbonate addition and stirring for 45 minutes; D: Wash-off – Cold rinse; E: Neutralization wash with acetic acid; F: Warm wash; G: Soaping; H: Hot rinse; I: Cold rinse.

Fenton oxidation

Wash-off wastewater collected after each dyeing was mixed and subjected to Fenton oxidation by using a simple laboratory set-up that comprised a glass beaker (1,000 mL) placed on a stirring device at room temperature. pH of the samples were adjusted by using 0.5 M H_2SO_4 and 0.5 M NaOH. After that, pre-determined amounts of catalyst $FeSO_4.7H_2O$ and 30% w/w H_2O_2 were added to initiate the production of hydroxyl radicals. Sample solution was constantly stirred using a magnetic stirrer at 150 rpm for 20 min. The Fenton reaction is based on the yield of hydroxyl radicals by the combination of peroxide ions and ferrous ions in acidic conditions. According to Equation (1), the reaction is very fast at the initial stage due to rapid degradation of organic contaminants by hydroxyl radicals OH^{-} in the presence of high Fe^{2+} ions. At the second stage, the rate of reaction will decrease due to the reaction of the Fe^{3+} and H_2O_2 forming $HO_2^{\cdot}$ radicals (E = 1.65 V) which are weaker oxidants compared to the $OH^{\cdot}$ radicals (E = 2.80 V) (Equation (2)):

Table 2 | Dyeing process conditions

Step	Washing step	Temperature (°C)	Time (min)
1.	Cold rinse	30	10
2.	Neutralization with CH_3COOH	30	10
3.	Warm wash	50	10
4.	Hot wash	80	10
5.	Soaping	50	10
6.	Cold rinse	30	10

$$Fe^{2} + H_2O_2 \longrightarrow Fe^{3+} + OH^{-} + OH^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 \longrightarrow Fe^{2+} + HO_2^{\bullet} + H^{+} \quad (2)$$

$$Fe^{3+} + HO_2^{\bullet} \longrightarrow Fe^{2+} + O_2 + H^{+} \quad (3)$$

$$OH^{\bullet} + H_2O_2 \longrightarrow HO_2^{\bullet} + H_2O \quad (4)$$

$HO_2^{\cdot}$ radical can reduce Fe^{3+} and hydroxyl radical reacts with hydrogen peroxide to form $HO_2^{\cdot}$ and H_2O.

Table 3 | Characteristic of wash-off wastewater

Parameters	Before Fenton process	After Fenton process
pH	9–10	2.8–3.0
COD (ppm)	1,200–1,700	400–600
TDS (ppm)	2,000–4,000	3,000–4,500
EC (μS/cm)	1,500–1,700	1,700–1,900

Percentage color removal was determined by using a UV/VIS spectrophotometer with the following equation:

$$\%\text{Color removal} = (A_0 - A)/A_0 \times 100 \tag{5}$$

where A_0 = absorbance untreated wash-off liquor, A = absorbance of Fenton treated wash-off liquor. The characteristics of wash-off wastewater are summarized in Table 3.

Reuse of treated wastewater

After Fenton oxidation, wastewater was reused in the next wash-off of the sample dyed fabric (5 g swatch) for each dye and this fabric was labeled as batch.

Testing protocols

Dyed samples obtained from standard dyeing and those using Fenton treated wastewater were subjected to color and wash fastness testing methods to evaluate the quality of material for commercial and domestic use. Testing results obtained for both fabrics dyed in fresh water and Fenton treated wastewater were compared. The reflectance values of samples were determined employing a 600 Datacolor Spectroflash spectrophotometer (USA) under illuminant D65, using 10° standard observer. Color values (lightness L*, red/green axis a*, yellow/blue b*, chroma C* and hue h) will be calculated and total color differences (color difference ΔE*, lightness difference ΔL*, chroma difference ΔC*, and hue difference Δh*) was determined using the following CMC equation:

$$\Delta E^{*}\text{cmc} = [(\Delta L^{*})^2 + (\Delta h^{*})^2 + (\Delta C^{*})^2]^{1/2} \tag{6}$$

Fastness properties of dyed fabrics for washing and rubbings were evaluated according to AATCC test methods 61-2001 (Colorfastness to Washing), and 8-2001 (Colorfastness to Crocking) were followed because these are commonly used in the industry. Grey scale 1 (poor) to 5 (excellent) was used for wash fastness properties.

RESULTS AND DISCUSSION

Fenton treatment results

Effect of pH on color removal

Fenton oxidation strongly depends on the pH of the sample solution due to the generation of hydrogen peroxide radical factors. Thus sufficient control of pH would increase efficiency of the reaction. The optimum pH for the Fenton reaction was found to be around 3 (Ebrahiem *et al.* 2017), regardless of the dye used, as shown in Figure 2. At higher pH activity, Fenton reagent is reduced due to the consumption of hydroxyl radical and formation of ferric hydroxide precipitate. The oxidation potential of hydroxyl radicals decreases with increasing pH. At pH below 3, formation of iron complex species $[Fe(H_2O)_6]^{2+}$, reacts slower with hydrogen peroxide than other species and results in deceased efficiency. At higher pH, the Fenton process is replaced by the coagulation process as the ferric ions present in solution precipitated in the form of ferric hydroxide ($Fe(OH)_3$).

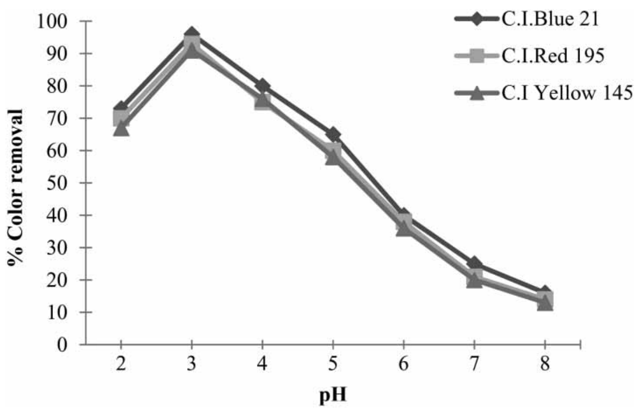


Figure 2 | Effect of pH on % color removal.

Effect of ferrous ion concentration on color removal

Laboratory scale studies to optimize the dose of ferrous ions to mineralize the organics is essential as a high amount of unutilized iron ions will increase the total dissolved solids (TDS) of effluent and it may render the reuse of wastewater (de Luna *et al.* 2013). Usually the rate of dye degradation increases with an increase in the concentration of ferrous ion up to a certain concentration and above the optimum dose a limited degradation rate will be observed. At the optimum dosage of ferrous ions, the percentage color removal achieved is 96, 95 and 93% for C.I. Blue 21, C.I. Red 195 and C.I. Yellow 145, respectively, as shown in Figure 3.

Effect of H_2O_2 concentrations on color removal

The concentration of hydrogen peroxide plays a central role for the overall efficiency of the dye degradation process. Usually the percentage color removal increases with an increase in the dosage of hydrogen peroxide. However, an excess amount is not suggested as the unused portion of hydrogen peroxide during the Fenton process contributes to COD, as shown in Figure 4, by using 2,000 mg/L of H_2O_2 color removal of 96, 95 and 93% is obtained for C.I. Blue 21, C.I. Red 195 and C.I. Yellow 145, respectively.

Evaluation of color strength

Color strength of standard and batch samples were compared in terms of k/s values as shown in Table 4, which was measured by using a Datacolor SF 600 spectrophotometer (USA). Δ k/s values were studied by using the following equation:

$$\Delta k/s = k/s\ (\text{standard}) - k/s\ (\text{batch}) \quad (7)$$

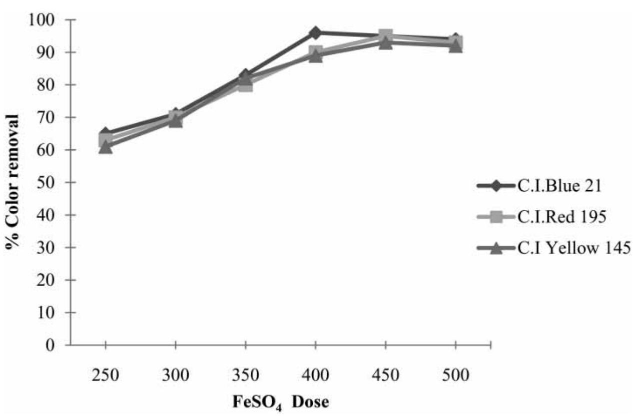


Figure 3 | Effect of Fe^{+2} concentrations on % color removal.

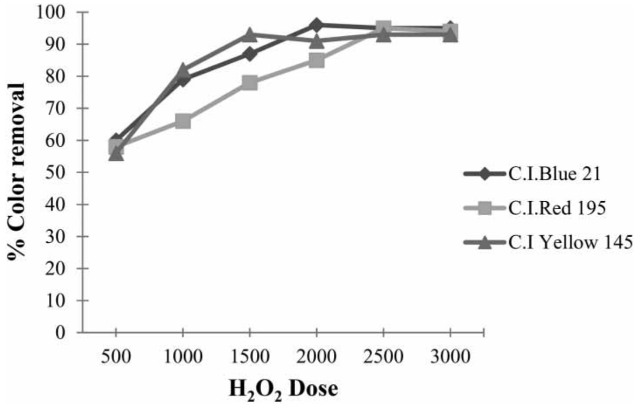


Figure 4 | Effect of H_2O_2 concentration on % color removal.

Table 4 | Comparison of k/s values of standard and batch samples

Dye	k/s value (standard)	k/s value (batch)	Δ k/s
C.I. Blue 21	25	26	1
C.I. Red 195	14.1	14.1	0
C.I. Yellow 145	21.5	18.9	2.6

Evaluation of color difference properties

Color difference values of dyed fabric between standard (dyed in fresh water) and batch (those wash-off using Fenton treated wastewater) samples were compared. Color difference in terms of ΔL*(lightness/darkness), Δc* (weaker/stronger), Δh*(hue difference) and ΔE*cmc (total color difference) results are shown in Table 5. If the value is positive, it means the color of the batch sample is lighter

Table 5 | CIELAB Color difference values of standard and samples dyed in Fenton treated wastewater

	CIELAB color difference values					
Dyes	ΔL*	Δa*	Δb*	Δc*	Δh*	ΔE*cmc
C.I. Blue 21	−1.66	−0.06	0.28	−0.14	−0.25	0.77
C.I. Red 195	−0.01	−0.01	−0.01	0.0	−0.02	0.02
C.I. Yellow 145	0.06	−0.19	−2.31	−2.16	−0.83	0.89

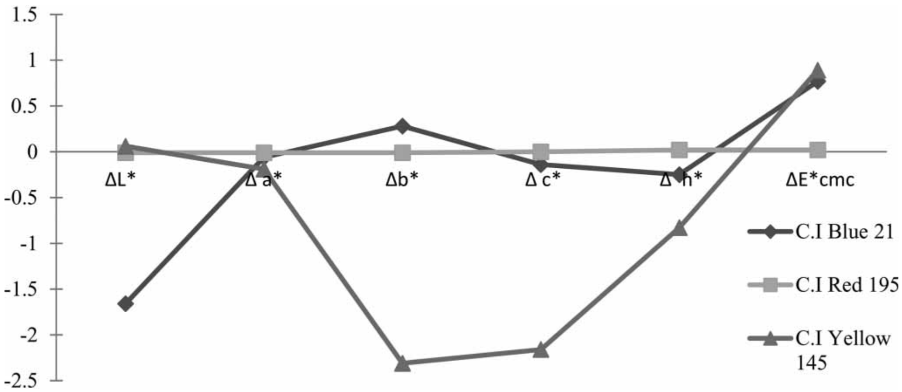


Figure 5 | Comparison of color fastness.

than the color of the standard, if the value is negative then it means the batch sample is darker than the standard. Δa* value indicates redder and greener tones of shade when the values are positive and negative, respectively. Similarly, a Δb* value indicates yellower and bluer tones of shade when the values are positive and negative, respectively. Table 5 also shows the magnitude of total color difference (ΔE*cmc), which is measured by a reflectance spectrophotometer and considered acceptable when the value is less than or equal to 1.0. C.I. Blue 21, ΔL* = –1.66 value indicated that the batch sample is darker than the standard and Δ c* = –0.14 showed a duller color. Δa* = –0.06 is greener and Δb* = 0.28 is bluer in shade. For C.I. Blue 21, the value of color difference (ΔE*) = 0.77 which is acceptable (Negueroles *et al.* 2017). It was observed in the case of C.I. Red 195 that the value of ΔE* was close to zero which means both sample and batch have negligible color difference. The Yellow 145 sample was acceptable when ΔE* = 0.89. ΔL* showed a lighter trend with a value of 0.06 and its Δc* = –2.16. The sample was greener in shade as Δa* = –0.19 and bluer Δb* = –2.31. The overall results given in Figure 5 show that the total color difference (ΔE* cmc) values of almost all dyeing were found to be less than 1.0, which is a commercially acceptable limit.

Evaluation of wash fastness properties

Table 6 shows a comparison of wash fastness of both reference and fabric dyed in Fenton treated wash-off wastewater. The results indicated that dry and wet rubbing and staining to a multifibre strip showed identical wash fastness as the changes in shade were acceptable as all results were in the range of 4.5–5 (Hossain *et al.* 2017). The dry and wet crocking results are provided in Table 7. The good fastness values and low difference in color confirmed that Fenton treated wastewater would be an acceptable option to using Fenton

Table 6 | Wash fastness properties of standard and samples dyed in Fenton treated wastewater

		Multi-fiber staining					
Dyes	**Type of dyeing**	**Celulose acetate**	**Unmercerized cotton**	**Nylon 6,6**	**Polyester terylene**	**Acrylic (courtelle)**	**Wool worsted**
C.I. Blue 21	Standard	5	4	4.5	4.5	4.5	4.5
C.I. Blue 21	Batch	5	4	4.5	4.5	4	4.5
C.I. Red 195	Standard	5	4	5	5	5	4.5
C.I. Red 195	Batch	5	5	4	5	5	5
C.I. Yellow 145	Standard	5	4	4.5	4.5	5	4.5
C.I. Yellow 145	Batch	5	4	5	5	5	4.5

Table 7 | Color strength properties of standard and samples dyed in Fenton treated wastewater

		Crocking	
Dye	Type of dyeing	DRY	Wet
C.I. Blue 21	Standard	4.5	4.5
	Batch	4.5	4.5
C.I. Red 195	Standard	4.5	4.5
	Batch	4.5	4.5
C.I. Yellow 145	Standard	4.5	4.5
	Batch	4.5	4.5

treated wastewater in the wash-off process to remove hydrolyzed dyes effectively.

CONCLUSIONS

In this research work, the ability of Fenton reagent to treat wash-off wastewater was tested. The color removal capacity of real wastewater of 12 dyes was investigated by optimizing reaction conditions such as pH, ferrous iron concentration and H_2O_2 concentration. This treatment proved to be very effective for color removal under acidic pH.

The present study investigated a new method of cotton dyeing wash-off using discarded wastewater which was generated during the washing and rinsing processes of reactive dyeing. A composite sample of the lab scale dyeing wash-off step was collected, and then treated using the Fenton oxidation process employing appropriate quantities of $FeSO_4$ and H_2O_2. At acidic pH (3), the Fenton process yielded a significant reduction (80–99%) of color. Several dyeing using three different types of dyes were carried out in Fenton decolorized wastewater, and commercially acceptable quality results in terms of wash fastness, crocking fastness, and color difference properties were attained. Experimental results indicated that ΔE^* values of all dyeing were found to be closer to 1.0, which is considered to be a commercially acceptable tolerance level in the industry. The present study also showed excellent results with reference to water saving and reduction of pollution load because the new method under investigation did not use any fresh water and used only discarded wastewater which could otherwise pollute water bodies. This study concluded that Fenton oxidation is an effective and efficient method of recycling spent liquor or wastewater from textile mills.

REFERENCES

Akali, N. M., Nyongesa, N. D., Neyole, E. M. & Miima, J. B. 2011 Effluent discharge by mumias sugar company in Kenya: an empirical investigation of the pollution of river Nzoia. *Sacha J. Environ. Stud.* **1** (1), 1–3.

Beltran, F. J., Gonzalez, M., Ribas, F. J. & Alvarez, P. 1998 Fenton reagent advanced oxidation of polynuclear aromatic hydrocarbons in water. *Water Air Soil Pollut.* **105** (3–4), 685–700.

Bes-Piá, A., Mendoza-Roca, J. A., Alcaina-Miranda, M. I., Iborra-Clar, A. & Iborra-Clar, M. I. 2002 Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies. *Desalination* **149** (1–3), 169–174.

Broadbent, A. D., Therien, N. & Zhao, Y. 1998 Comparison of the thermal fixation of reactive dyes on cotton using infrared radiation or hot air. *Ind. Eng. Chem. Res.* **37** (5), 1781–1785.

Burkinshaw, S. M. & Salihu, G. 2018 The role of auxiliaries in the immersion dyeing of textile fibres: part 10 the influence of inorganic electrolyte on the wash-off of reactive dyes. *Dyes Pigm.* **149**, 652–661.

Christensen, A., Gurol, M. D. & Garoma, T. 2009 Treatment of persistent organic compounds by integrated advanced oxidation processes and sequential batch reactor. *Water Res.* **43** (16), 3910–3921.

de Luna, M. D. G., Colades, J. I., Su, C. C. & Lu, M. C. 2013 Comparison of dimethyl sulfoxide degradation by different Fenton processes. *Chem. Eng. J.* **232**, 418–424.

Ebrahiem, E. E., Al-Maghrabi, M. N. & Mobarki, A. R. 2017 Removal of organic pollutants from industrial wastewater by applying photo-Fenton oxidation technology. *Arab. J. Chem.* **10**, 1674–1679.

El Qada, E. N., Allen, S. J. & Walker, G. M. 2008 Adsorption of basic dyes from aqueous solution onto activated carbons. *Chem. Eng. J.* **135** (3), 174–184.

Erdumlu, N., Ozipek, B., Yilmaz, G. & Topatan, Z. 2012 Reuse of effluent water obtained in different textile finishing processes. *AUTEX Res. J.* **12** (1), 23–28.

Ertugay, N. & Acar, F. N. 2017 Removal of COD and color from Direct Blue 71 azo dye wastewater by Fenton's oxidation: kinetic study. *Arab. J. Chem.* **10**, 1158–1163.

Gogate, P. R. & Pandit, A. B. 2004 A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions. *Adv. Environ. Res.* **8** (3), 501–551.

Gokkuş, O., Çoşkun, F., Kocaoglu, M. & Yldz, Y. S. 2014 Determination of optimum conditions for color and COD removal of Reactive Blue 19 by Fenton oxidation process. *Desal. Water Treat.* **52** (31–33), 6156–6165.

Hofl, C., Sigl, G., Specht, O., Wurdack, I. & Wabner, D. 1997 Oxidative degradation of AOX and COD by different advanced oxidation processes: a comparative study with two samples of a pharmaceutical wastewater. *Water Sci. Technol.* **35** (4), 257–264.

Hossain, M. D., Khan, M. M. R. & Uddin, M. Z. 2017 Fastness properties and color analysis of natural indigo dye and compatibility study of different natural reducing agents. *J. Polym. Environ.* **25** (4), 1219–1230.

Hu, E., Shang, S., Tao, X., Jiang, S. & Chiu, K. L. 2018 Minimizing freshwater consumption in the wash-off step in textile reactive dyeing by catalytic ozonation with carbon aerogel hosted bimetallic catalyst. *Polymers* **10** (2), 193–211.

Lou, J. C. & Huang, Y. J. 2009 Assessing the performance of wastewater treatment with the combination of Fenton and ferrite process. *Environ. Monit. Assess.* **151** (1–4), 251–258.

Lu, M. C., Lin, C. J., Liao, C. H., Huang, R. Y. & Ting, W. P. 2003 Dewatering of activated sludge by Fenton's reagent. *Adv. Environ. Res.* **7** (3), 667–670.

Lu, X., Liu, L., Liu, R. & Chen, J. 2010 Textile wastewater reuse as an alternative water source for dyeing and finishing processes: a case study. *Desalination* **258** (1), 229–232.

Mangat, A., Shaikh, I. A., Ahmed, F., Munir, S. & Baqar, M. 2014 Fenton oxidation treatment of spent wash-off liquor for reuse in reactive dyeing. *Tech. J. Taxila* **19** (4), 43–47.

McMullan, G., Meehan, C., Conneely, A., Kirby, N., Robinson, T., Nigam, P. & Smyth, W. F. 2001 Microbial decolourisation and degradation of textile dyes. *Appl. Microbiol. Biotechnol.* **56** (1–2), 81–87.

Negueroles, P. G., Bou-Belda, E., Santos-Juanes, L., Amat, A. M., Arques, A., Vercher, R. F. & Vicente, R. 2017 Treatment and reuse of textile wastewaters by mild solar photo-Fenton in the presence of humic-like substances. *Environ. Sci. Pollut. Res.* **24** (14), 12664–12672.

Oller, I., Malato, S. & Sánchez-Pérez, J. 2011 Combination of advanced oxidation processes and biological treatments for wastewater decontamination – a review. *Sci. Total Environ.* **409** (20), 4141–4166.

Patel, M. N. & Shah, M. 2013 Feasibility study of Fenton method for the treatment of dyeing and printing mill wastewater. *Int. J. Sci. Eng. Technol.* **2** (5), 411–416.

Perez, M., Torrades, F., Domenech, X. & Peral, J. 2002 Fenton and photo-Fenton oxidation of textile effluents. *Water Res.* **36** (11), 2703–2710.

Pierce, J. 1994 Colour in textile effluents – the origins of the problem. *Color. Technol.* **110** (4), 131–133.

Rauf, M. A., Shehadi, I. A. & Hassan, W. W. 2007 Studies on the removal of Neutral Red on sand from aqueous solution and its kinetic behavior. *Dyes Pigm.* **75** (3), 723–726.

Shafeeyan, M. S., Pouran, S. R., Bayrami, A., Raman, A. A. A. & Daud, W. M. A. W. 2018 A comparative study on a cationic dye removal through homogeneous and heterogeneous Fenton oxidation systems. *Acta Chim. Slov.* **65** (1), 166–171.

Shaikh, I. A., Ahmed, F., Sahito, A. R. & Pathan, A. A. 2014 In-situ decolorization of residual dye effluent in textile jet dyeing machine by ozone. *Pak. J. Anal. Environ. Chem.* **15** (2), 71–76.

Sin, J. C., Lam, S. M. & Mohamed, A. R. 2011 Optimizing photocatalytic degradation of phenol by TiO 2/GAC using response surface methodology. *Korean J. Chem. Eng.* **28** (1), 84–92.

Sindhi, Y. & Mehta, M. 2014 COD removal of different industrial wastewater by Fenton oxidation process. *J. Eng. Sci. Res. Technol.* **3** (3), 1134–1139.

Sohrabi, M. R., Khavaran, A., Shariati, S. & Shariati, S. 2017 Removal of Carmoisine edible dye by Fenton and photo Fenton processes using Taguchi orthogonal array design. *Arab. J. Chem.* **10**, 3523–3531.

Tunc, S., Gurkan, T. & Duman, O. 2012 On-line spectrophotometric method for the determination of optimum operation parameters on the decolorization of Acid Red 66 and Direct Blue 71 from aqueous solution by Fenton process. *Chem. Eng. J.* **181**, 431–442.

Zhu, W., Yang, Z. & Wang, L. 1996 Application of ferrous-hydrogen peroxide for the treatment of H-acid manufacturing process wastewater. *Water Res.* **30** (12), 2949–2954.

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