Fenton Oxidation Treatment of Spent Wash-Off Liquor for Reuse in Reactive Dyeing

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Abstract-The use of clean and high quality water in textile dyeing process is very expensive. In this study, the potential of reusing Fenton treated wash-off wastewater generated at the end of reactive dyeing was investigated. The treated wastewater was used in several dyeings employing three widely used reactive dyes, C. I. Reactive Yellow 145, C. I. Reactive Red 194, and C. I. Reactive Blue 221. Experimental results showed that at acidic pH (3.5) using optimized quantities of $FeSO_4$ and H_2O_2, Fenton process yielded a significant reduction (80-99%) of colour and COD in 30 minutes of treatment time. New dyeings were then carried out in Fenton decolourized wash-off wastewater, and dyed fabric samples were subjected to quality evaluations in terms of wash fastness, crock fastness, and colour difference properties (ΔL^*, Δc^*, Δh^*, and ΔE^*). This study concluded that Fenton oxidation was an efficient method for the treatment of textile wash-off wastewater, and treated liquor can be effectively recycled in next dyeing, without compromising quality parameters. This method proved to be an eco-friendly process owing to the fact that it did not use any fresh water.

Keywords-Fenton, Reactive Dye, Wash-off, Wastewater, Fastness

I. INTRODUCTION

In the nature, just like energy, water is neither created nor destroyed, but it can be converted from one form to another. In the natural water cycle, rain falling on the land is mostly transpired by the plantation. However, some portion of the water also infiltrates into the groundwater, and some runs off to the rivers and flows to the oceans to evaporate, and comes back as rain. Approximately, all of the world's water (97%) occurs as salted or brackish water, and of the remaining 3%, two-thirds occurs as ice and snow. Thus, merely about 1% of global water is available as liquid freshwater. Higher than 98% of the freshwater is available as groundwater, while less than 2% is available in lakes and streams. All this proves that liquid freshwater is a limited and finite natural resource [i].

Contamination of surface and ground water because of the direct discharge of partially treated or completely untreated industrial and domestic sewage has increased drastically. However, with the existing conventional treatment methods, it is now possible to decrease the organic load in terms of chemical oxygen demand (COD) and biological oxygen demand (BOD) , but not the pollution load in terms of colour and inorganic.

Textile wet processing sector, water is extensively used in almost every step of a variety of processes, both to transfer the required dyes and chemicals from the liquor to the textile materials and to wash them out once the chemical process is completed. Consequently, textile sector (particularly dyeing, finishing, and printing) is responsible for the release of huge quantity of highly coloured effluent into natural waterways. A normal reactive dyeing process uses about 120 to 280 litres of fresh water for every kilogram of textile processed [ii]. In reactive dyeing method, rinsing and washing-off steps are highly water-intensive because these processes usually account for almost 50% of the total dyeing cost and effluent load [iii].

Effluent from textile bleaching, dyeing and finishing processes having chemical oxygen demand (COD) concentration higher than 1600 mg/l and a strong dark colour is characterized as high strength wastewater. It is a significant source of environmental pollution. Moreover, this wastewater contains detergents, oil, suspended and dissolved solids, high pH, high temperature, toxic and non-biodegradable matter, and alkalinity. The coloured effluents also pose serious ecological threats; for example, they drastically affect the photosynthetic action of aquatic plants by stopping light penetration. Many dyes and pigments are complex aromatic compounds and are difficult to dispose of by natural remediation. Azo dyestuff are found to be resistant to biodegradation and removal of reactive dyes from effluents is a difficult task because of their high solubility [iv].

A solution to convert textile processes more environment friendly and less water intensive is wastewater recycling which can bring major environmental benefits by reducing water consumption and contaminants discharge. A number of wastewater treatments are available which involve physical, chemical, and biological methods, and numerous possible combinations of these methods [v]. Most widely practised treatments include coagulation, flocculation, precipitation, sedimentation, filtration, activated sludge, trickling filter, and chlorination. The major drawbacks of these conventional treatments include inefficiency, higher cost of operation, and requirement of large land [vi].

Advanced oxidation processes (AOPs) rely on in-situ production of highly reactive hydroxyl radicals (·OH) which possess highest oxidation power. Comparisons of oxidizing potential of different oxidizing agents are displayed in Table I. Fenton based oxidation treatment is considered as one of the oldest advanced oxidation processes (AOPs). In this method, hydroxyl (OH) radicals are produced directly at acidic pH. These powerful hydroxyl radicals (E0=2.8 V) can entirely degrade organic materials to CO_2 and H_2O [vii].

TABLE I
COMPARISON OF OXIDATION POTENTIAL OF SEVERAL OXIDIZING AGENTS

Oxidizing Agent	Oxidation Potential (V)
Hydroxyl Radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen	1.23

The Fenton process ($FeSO_4.7H_2O$ and H_2O_2) is more simply operated and maintained than other AOPs. Fenton oxidation is carried out via four stages which include pH adjustment (around 3-4), oxidation reaction, neutralization and coagulation [viii]. When pH of the wastewater is set around 3.50 during Fenton oxidation, it yields higher degree of decolourization due to the stability of hydrogen peroxide (H_2O_2) and ferrous ions in this pH range [ix]. However, if the pH values of liquor are set higher than 4.0, ferrous ions are converted to ferric ions and, consequently, ferric hydroxo complexes are produced. H_2O_2 is found to be unstable and decomposes itself in the basic (pH> 10) medium [x].

The main reactions involved in Fenton oxidations are shown in equations 1- 4 [xi]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO \quad (1)$$

$$Fe^{3+} + H_2O_2 \leftrightarrow H^+ + [Fe(OOH)]^{2+} \quad (2)$$

$$[Fe(OOH)]^{2+} \rightarrow Fe^{2+} + HO_2\cdot \quad (3)$$

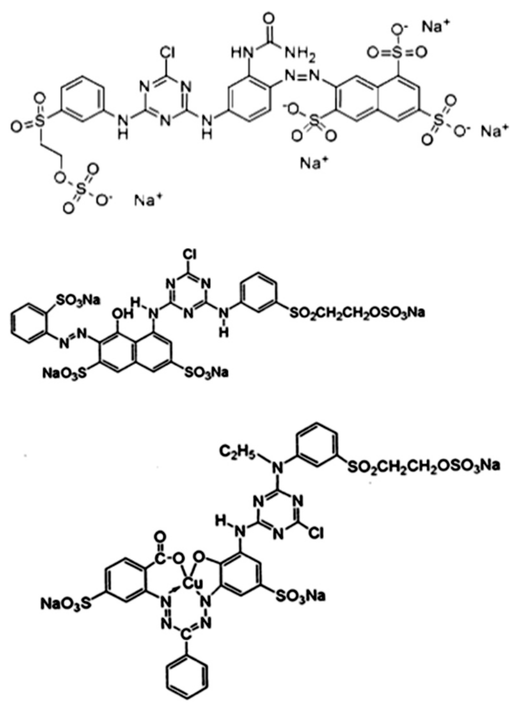
$$HO_2\cdot + Fe^{3+} \rightarrow Fe^{2+} + H^+ + O_2 \quad (4)$$

In this research, discarded washing and rinsing wastewater generated at the end of reactive dyeing was collected and treated using Fenton oxidation in order to remove colour from the wastewater for possible reuse in reactive dyeing. The results obtained in this study suggested that Fenton oxidation was a promising technique to treat spent wash-off liquor for recycling purpose. Moreover, this process proved to be an eco-friendly process because it did not use any fresh water in the process, and thus decreased pollution load significantly.

II. MATERIALS AND METHODS

2.1 Materials

Knitted fabric (single jersey) made with 100% cotton 30/s combed ring-spun yarn having 200 g/m2 was used throughout the study. Three widely used reactive dyes, C. I. Reactive Yellow 145, C. I. Reactive Red 194, and C. I. Reactive Blue 221 were used in the experimental work. Chemical auxiliaries like Na2SO4 and NaOH were used of commercial grade, without any purification. Fig. 1 shows the chemical structures of bi-functional (vinylsulphone/ monochlorotriazine) dyes used in the study.



(a) (b) (c)

Fig. 1. Structures of dyes used (a) C. I. Reactive Yellow 145 (b) C. I. Reactive Red 194 (c) C. I. Reactive Blue 221

2.2 Wastewater Analysis

Equal quantities of wastewater from various washing and rinsing stages of reactive dyeing were collected directly from the drain of the dyeing machine, and a composite sample of wastewater was prepared. Physical and chemical properties of this wastewater were determined before giving Fenton oxidation. The results are displayed in Table II. The results showed that major issue with the wastewater was COD as its results (205ppm) were exceeded national environment quality standards (NEQS), which is 150ppm. Biological oxygen demand (BOD) value was obtained as 27ppm which was under NEQS requirements of 80ppm. The higher conductivity value (146 µS/cm) indicated presence of salt (either NaCl or Na_2SO_4). Another issue noticed with the wastewater before Fenton oxidative treatment was its dark colour in grey and black tone. This shows that dye residues from the previous dyeing were carried out to washing and rinsing process. Without giving any treatment to this wastewater, correct dyeing with acceptable quality parameters is not expected.

TABLE II
CHARACTERISTICS OF WASHING EFFLUENT

Constituents	Concentration
Chemical oxygen demand (COD)	205 ppm
Biological oxygen demand (BOD)	27 ppm
Chlorides	9 ppm
pH	8.8
Conductivity	146 µS/cm
Colour	Grey/black

2.3 Fenton Oxidation

Spent wash-off liquor was subjected to Fenton oxidation using a simple laboratory set-up that was comprised of a glass beaker (1000 ml capacity) placed on a stirring device. The volume of effluent in each experiment was 0.50 litre. Optimum doses of ferrous sulfate ($FeSO_4 7H_2O$) and hydrogen peroxide (H_2O_2) were selected as 200 mg/L and 400 mg/L, respectively. The pH of the liquor was set at 3.50, and the Fenton oxidation continued for 30 minutes at ambient temperature (35°C). These recommendations were chosen based on previous studies [vii,ix,xii].

2.4 Dyeing Procedure

The dyeing of fabrics, using Fenton decolorized wash-off wastewater, was carried out in AHIBA NUANCE (Datacolor, USA) dyeing machine. Prepared for dyeing fabric samples (10 gram each) of single jersey (knitted) constructions were dyed using a liquor ratio (L:R) of 1:8. The dyeing process is shown in Fig. 2. Since it was an isothermal dyeing process, the whole of dyeing took place at 60°C. Salt and dyes were added after 5 minutes of process start-up, and it continued for 30 minutes until pre-dissolved alkali was added to the dyeing bath. A further 60 minutes dyeing was continued so that fixation process is completed. At the completion of dyeing process, dyed samples were withdrawn from the machine, rinsed thoroughly in cold water to remove salt. The 2nd warm wash using 1 g/l of acetic acid was given to dyed samples in order to neutralize residues of alkali and to bring the pH of bath down to neutral. The 3rd and 4th washes were comprised of 1 g/l detergent and hot water (80-90°C) to remove unfixed and hydrolyzed dyes from the dyed fabric which could otherwise stain adjust fabrics during washing tests. Finally, the fabrics were removed from the dyeing machine, and dried in the dryer using hot air. A conditioning time of 24 hrs was given to dyed samples before they were assessed for colour difference and fastness properties.

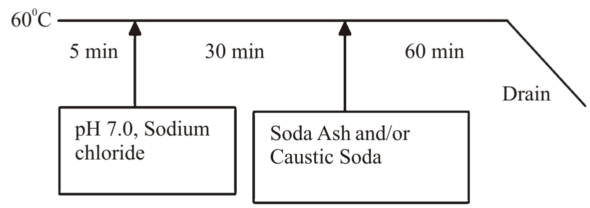


Fig. 2. Dyeing method used in the study

2.5 Testing Protocols

Dyed samples obtained from standard dyeing and those using Fenton treated wastewater were subjected to various testing methods required to assess 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 Datacolor Spectroflash 600 spectrophotometer under illuminant D65, using 10 degree standard observer, with specular component excluded and UV component included. The samples were folded twice in order to achieve four thicknesses, and the average of four measurements was taken for every dyed sample.

Using an ultraviolet Perkin Elmer LAMBDA 25 UV/Vis spectrophotometer , the absorbance of liquor was Calculated under the maximal absorption peak (λ max) of the dye solution, which was adjusted to neutral pH (7.0) by diluted acetic acid. The decolourization ratio of liquor before and after Fenton oxidation was determined using calculated using equation 5.

$$D\,(\%) = \frac{A_0 - A_1}{A_0} \times 100 \qquad (5)$$

Where D (%) is colour removal efficiency, A_0 was the absorbance of untreated spent wash-off liquor and A_1 was the absorbance of the Fenton treated wash-off liquor. Fastnesses properties of dyed fabrics for washing and rubbings were evaluated according to ISO 105 C06 method (A1S) and ISO 105-X12, respectively. The colour fastness is usually expressed either by depth or loss of colour in dyed samples or it expressed by staining scale. Wash fastness of dye is influenced by the rate of diffusion of dye and state of dye inside the textile materials [xiii]. The washing fastness test was conducted by washing dyed samples using 1 g/L of non-ionic soap.

III. RESULTS AND DISCUSSION

3.1 Removal of Colour and COD

Table III exhibits colour and COD removal efficiency of Fenton oxidation for composite wastewater sample comprised of equal amount of used wash-off liquors from various washing steps, mainly, cold rinsing, neutralization, hot washing, soaping-off, and final rinsing. In all cases, the amount of ferric sulphate ($FeSO_4$) was kept at 100 ppm due to the cost factor. It was evident from the results that Fenton process was highly efficient method of removing colour and COD, with colour removal efficiencies up to 99%. When H_2O_2 concentration was set to 100mg/L, lower values of COD removal (52%) and decolourization (64%) were achieved. However, when H_2O_2 concentration were increased to 500 mg/L, the COD and colour removal efficiencies reached to 79 and 99%, respectively. Overall results indicated an increase in COD and colour removal when H_2O_2 concentrations were increased.

TABLE III
COLOR AND COD REMOVAL RESULTS OF FENTON PROCESS

Dose of H_2O_2 (mg/L)	pH	$FeSO_4$ (mg/L)	Temp. ^oC	COD (mg/L)	Colour Removal (%)
100	3.50	100	35	52	64
200				59	75
300				65	81
400				77	97
500				79	99

3.2 Evaluation of Colour Difference Properties

Table IV displays colour difference values in terms of lightness/darkness (ΔL*), weaker/stronger (Δc*), hue difference (Δh*) and magnitude of total colour difference (ΔE*). These values compared the colour properties of standard fabric (dyed in fresh water) with those dyed using Fenton treated wash-off wastewater. Overall results showed that total colour difference (ΔE*) values of all three dyeing were found to be less than 1.0, which showed commercially acceptable tolerance level [x]. In case of C. I. Reactive Yellow 145, ΔE* value of 0.34 confirmed that the final shade of the sample dyed using Fenton treated wastewater was comparable to that of reference sample. For C. I. Reactive Red 194 dyed fabric, negligible colour differences in lightness (ΔL*= -0.38), chroma (Δc*= -0.17), hue (Δh* = 0.44), and total difference (ΔE* =0.75) indicated an identical colour match. Similar trend was seen in case of C. I. Reactive Blue 221 dye. However, in all cases a bit duller shade was observed in shades obtained using Fenton treated wastewater. These results can be attributed to the presence of metallic impurities due to the use of $FeSO_4$.

3.3 Evaluation of Fastness Properties

TABLE IV
COLOUR DIFFERENCE VALUE OF STANDARD AND SAMPLES DYED IN FENTON TREATED WASTEWATER

Dyes	Colour difference values					
	ΔL^*	Δa^*	Δb^*	Δc^*	Δh^*	ΔE^*
C. I. Reactive Yellow 145	-0.31	0.15	0.16	0.09	0.22	0.34
C. I. Reactive Red 194	-0.48	0.29	0.22	-0.17	0.44	0.75
C. I. Reactive Blue 221	-0.70	0.34	-0.29	-0.37	-0.11	0.51

Table V shows fastness properties of both reference and samples dyed in Fenton treated wash-off effluent. The overall results showed that all fabric samples yielded similar fastness ratings compared to those of standard dyed fabrics. The colour fastness results of C.I. Reactive Yellow 145 dye displayed results in the range of 4.5 to 5.0, which are considered excellent in the industry [xiv]. For C. I. Reactive Red 194 and C. I. Reactive Blue 221 dyes, fastness results pertaining to dry and wet rubbing, staining to cotton, nylon, and polyester were found to be acceptable and comparable to those of reference samples. The values of change in shade were also found to be excellent because all result were limited to 4.5 or 5.0, which is the indication of very low difference in colour. These values also coorolated the results obtained in terms ΔL*, Δc*, and ΔE*.

TABLE V
WASH FASTNESS PROPERTIES OF REFERENCE AND SAMPLES DYED IN FENTON TREATED WASTEWATER

Dyes	Rubbing Fastness		Multi-fibre staining			Shade change
	Dry	Wet	Cotton	Nylon	Polyester	
Reference	5	4.5	4.5	5	5	-
C.I. Reactive Yellow 145	5	4.5	4.5	5	5	5
C. I. Reactive Red 194	5	4.5	4.5	5	5	4.5
C. I. Reactive Blue 221	5	4.5	4.5	5	5	4.5

IV. CONCLUSION

The present study investigated a new method of cotton dyeing using discarded wastewater which was generated during washing and rinsing processes of reactive dyeing. Composite sample of real wastewater coming from textile wash-off step was collected from a production facility, and then treated using Fenton oxidation process employing appropriate quantities of $FeSO_4$ and H_2O_2. At acidic pH (3.5), Fenton process yielded a significant reduction (80-99%) of colour and COD in only 30 minutes of reaction time. Several dyeings using three different types of dyes were carried out in Fenton decolourized wastewater, and commercially acceptable quality results in terms of wash fastness, crocking fastness, and colour difference properties were attained. Experimental results indicated that ΔE* values of all dyeing were found to be closer to 1.0, which is considered 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 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.

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