Performance Evaluation of Fenton Oxidation Treatment Method for the Reuse of Reactive Dyeing Effluent

Sana Islam*, Irfan Ahmed Shaikh, Nabeela Firdous, Azhar Ali and Yumna Sadef
College of Earth & Environmental Sciences, University of the Punjab, Lahore (54590).
islamsana86@gmail.com; textilemaster@gmail.com*

(Received on 3rd April 2018, accepted in revised form 22nd March 2019)

Summary: In this study, a novel wash-off method was investigated wherein the use of Fenton's reagent was evaluated to get rid of hydrolyzed and unfixed reactive dyes from wash-off liquor and reused in next wash-off process. After dark shade dyeing (5% o.w.f) with C.I. Reactive Blue 72, C.I. Reactive Blue 221, C.I. Reactive Red 141, C.I. Reactive Red 198, C.I. Reactive Orange 84, C.I. Reactive Orange 122, C.I. Reactive Yellow 105 and C.I. Reactive Yellow 138 , fabrics were subjected to both clean water (reference) and treated wash-off liquors (batch) and comparisons were made. Fenton reagent was proved capable to achieve 88-97% color reduction in wash-off liquor at pH 3 by using optimal dose of $FeSO_4$ and H_2O_2 at room temperature. Then effectiveness of Fenton's reagent treated wash-off was evaluated in terms of color difference values (ΔL^*, ΔC^*, Δh^* and ΔE^*), wash fastness and crocking properties. For color fastness properties the commercially tolerable value of $\Delta E^* \leq 1$ was observed for blue and red dyes and slightly higher value for yellow and orange dyes. Wash fastness and crocking results are almost similar for reference and batch dyed fabrics and their values ranges 4-5 on grey scale. Color strength (K/S) showed negligible difference in values indicating that fabrics absorbed almost same amount of dyestuff for each dye .Fenton method of treatment proved to be an eco-friendly and economically feasible treatment method and treated liquor can be effectively used in next dyeing, without compromising quality parameters.

Key words: Washing-off, Reactive dyes, Fenton's reagent, Fastness, Color strength.

Introduction

Textile dyeing and finishing processes use huge volumes of water for preparation of final product [1]. In dyeing, wash-off process to remove unfixed dyestuffs consumes large quantities of water as well as generates huge volumes of wastewater. This polluted water contains residues of dyes, heat, suspended solids, and high COD and BOD [2, 3]. The untreated polluted water into receiving bodies adversely affects aquatic life and damage ecosystem by poor sunlight penetration [4]. Various techniques such as adsorption, coagulation, membrane separation, ozonation, photocatalysis were employed for the degradation of dyes from textile effluent. A variety of low cost adsorbents, like activated carbon, bottom ash and de-oiled soya were successfully used for treatment of dyes as shown in Table-1 [5]. Nowadays, Nanocomposites photocatalysts with short contact time and high adsorption capacity were synthesized like Fe_3O_4, V_2O_5/ZnO, ZnO/CuO, ZnO/Ag, titanium dioxide and competently used for the treatment of dyes in aqueous solutions [6-9].

Advance oxidation processes AOPs are considered as efficient alternative to conventional treatment methods as they produce highly reactive hydroxyl radicals which attack pollutants in the aqueous media [10, 11]. The use of advanced oxidation processes (AOPs) including Fenton's reagent has been successfully in practice for the elimination of various dyes from textile effluents. Fenton's reagent is found to be effective to achieve complete color and partial chemical oxygen demand (COD) removal from textile wastewater [12, 13]. Fenton's reagent is a mixture of H_2O_2 and ferrous (Fe^{+2}) ions in acidic medium that generate hydroxyl radicals (OH•) with oxidation potential = 2.8V. Fenton's process is simple and inexpensive process. This study utilized Fenton's oxidation for the decolorization of surface deposited unfixed reactive dyes on cotton fabric that causes poor washing fastness.

Several studies have suggested that after treatment of textile wastewater, it can be reused in other industrial processes [14-16]. Textile wastewater reclamation and reuse can conserve water and help in reduction of environmental pollution [17]. During dyeing, wash-off step is the most water consuming process. Hence, treatment and reuse of wash-off wastewater offers potential saving in water usage [14-16]. It is highly desirable to practice treatment and reuse of textile wastewater to attain zero liquid discharge. Eco–friendly low cost wastewater treatment and wastewater recycling cuts down the use of clean water in textile processing.

*To whom all correspondence should be addressed.

Table-1: Various reported adsorbent for synthetic dyes.

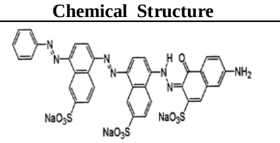
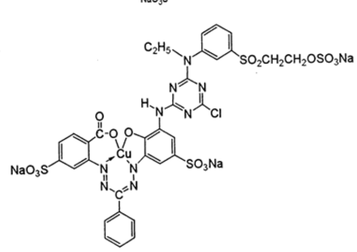
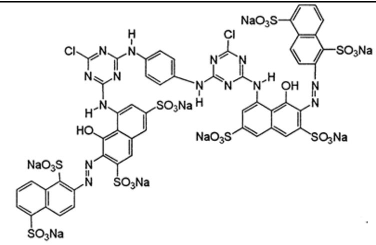
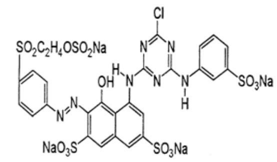
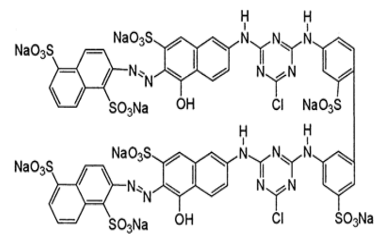
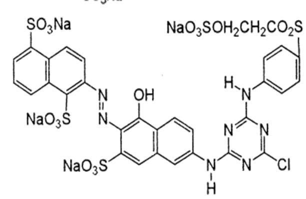
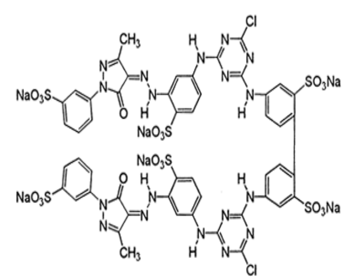
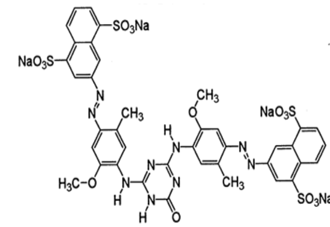
Adsorbent	Dye	Reference
Bottom ash/ De-oiled soya	**Chrysoidine Y**	**[5]**
Mesoporous carbon/ Titanium dioxide	**Methyl orange**	**[18]**
Titanium dioxide	**Tartrazine**	**[7]**
Persea americana nuts	**Eriochrome Black T**	**[19]**
Chitosan/Alumina composite	**Methyl Orange**	**[20]**
Coconut shell	**Malachite Green**	**[21]**
Hazelnut husks	**Methylene blue**	**[22]**
Pine fruit shell-carbon	**Methylene blue**	**[23]**
Bagasse	**Acid Blue**	**[24]**
Plant leaf powder	**Methylene blue**	**[25]**
Rice husk	**Acid Blue**	**[26]**
Walnut shell-carbon	**Methylene blue**	**[27]**
Aspergillus niger	**Direct red 28**	**[28]**
Oil palm shell-carbon	**Methylene blue**	**[29]**
Aspergillus niger	**Disperse red**	**[30]**
Wood apple rind-carbon	**Methylene blue**	**[31]**
Tree fern	**Basic Red 13**	**[32]**
Pine sawdust	**Acid Yellow 132**	**[33]**
Green alga	**Reactive red 5**	**[34]**
Peanut hull	**Reactive Black 5**	**[35]**

In present research work, a new wash-off method is investigated wherein spent wash-off liquor during dyeing was first subjected to Fenton's oxidation for complete decolorization. Afterwards; the decolorized wash-off wastewater was reused in the next wash-off process. This study will be useful in the conservation of fresh water.

Experimental

Already scoured and bleached 100% commercial cotton single jersey knitted fabric of 200 g/m^2 was used throughout experimental study. Eight synthetic reactive dyes used in the study are summarized in Table-2. Chemical auxiliaries like sodium chloride, sodium carbonate and sodium hydroxide of commercial grade were used in dyeing process and used without any prior purification. During wash-off process acetic acid (1g/L) was used for neutralization step and Dekol SN as soaping agent in the soaping step.

Table-2: Reactive dyes used in the experimental work.

CI Name	Chemical Structure
C.I. Reactive Blue 72	
C.I. Reactive Blue 221	
C.I. Reactive Red 141	
C.I. Reactive Red 198	
C.I. Reactive Orange 84	
C.I. Reactive orange 122	
C.I. Reactive Yellow 105	
C.I. Reactive Yellow 138	

Dyeing and washing-Off

Deep shade (5% o.w.f) dyeing was carried out individually for each dyestuff on 10-gram fabric sample, consisted of two swatches (5g each). The dyeing was done in an IR laboratory dyeing machine (Datacolor, USA) using liquor ratio of 1:10 by adding 80 g / L sodium chloride (NaCl) and 20 g/L of sodium carbonate (Na_2CO_3). All dyeing were carried out at 60°C for 60 minutes by using isothermal all-in-one laboratory method. After fixation phase, one fabric swatch was washed-off conventionally with clean water as shown in Table 3. This fabric swatch was used as reference. The other fabric swatch was washed-off with Fenton treated wastewater.

Table-3: Conventional Washing-off.

Step	Operation	Temp.(°C)	Time (min)
1	Cold rinse	25°C	10
2	Neutralization with Acetic Acid	25°C	10
3	Warm Wash	50°C	10
4	Hot Wash	80°C	10
5	Soaping / Boil-off	95°C	10
6	Cold rinse	25°C	10

Fenton Treatment

Wash-off wastewater was collected after each washing-off step and subjected to Fenton oxidation by using a simple laboratory set-up shown in Fig. 2. This was comprised of a glass beaker (1 liter capacity), placed on a stirring device. Colored wastewater was subjected to Fenton's process by using optimum dose of ferrous sulphate ($FeSO_4$) and hydrogen peroxide (H_2O_2) in acidic medium. For 500 ml wastewater 1 ml/l of hydrogen peroxide (30 %) and 250 ppm ferrous sulphate was used at pH 3 with 30 minutes of stirring at room temperature. The Fenton reaction is based on the generation of hydroxyl radicals ($OH^\bullet$) by combination of hydrogen peroxide and ferrous ions in acidic condition .According to Eq (a,b) reaction was very fast at initial stage due to rapid degradation of organic contaminants by hydroxyl radicals $OH^\bullet$ in the presence of high Fe^{2+} ions. At the second stage, the rate of reaction was decreased due to reaction of the Fe^{3+} and H_2O_2 forming $HO_2^\bullet$ radicals (E=1.65 V) which are weaker oxidants compared to the OH $^\bullet$radicals (E= 2.80 V) (Eq. (e))

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

$$Dye + OH^\bullet \longrightarrow Org + CO_2 + H_2O \quad (b)$$

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

$$OH^\bullet + OH^\bullet \longrightarrow H_2O_2 \quad (d)$$

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

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

$$OH^\bullet + H_2O_2 \longrightarrow HO_2^\bullet + H_2O \quad (g)$$

Eq. (f) and (g) shows $HO_2^\bullet$radical can reduce Fe^{3+} and hydroxyl radical reacts with hydrogen peroxide to form $HO_2^\bullet$ and H_2O.

Color removal efficiency was determined by using UV/VIS Spectrophotometer with following equation:

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

Where, A_0 = absorbance of untreated wash-off liquor, A = absorbance of Fenton treated wash-off liquor

After Fenton oxidation treatment, wash-off wastewater pH was adjusted to 7 and then used in the washing-off of remaining 5 g dyed samples which were labeled as batch. After wash-off, fabric samples were squeezed, dried, and conditioned for 24 hours before evaluation of color and wash fastness properties. All experiments were conducted at ambient temperature.

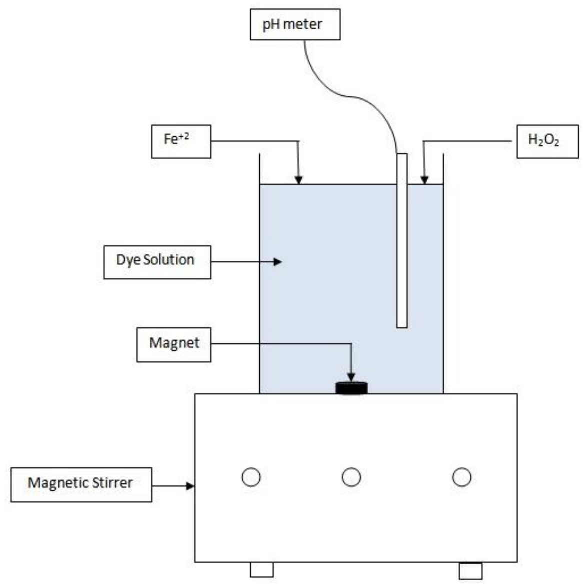


Fig. 1: Laboratory set-up for Fenton application.

Color fastness and shade evaluation

The color reflectance values of samples were calculated by using Spectraflash SF 600 PLUS CT spectrophotometer (Datacolor, USA). CIELAB color values (red/green axis a*, yellow/blue axis b*, lightness L*, chroma C* and hue h*) were estimated and color difference values (total color difference (ΔE*), lightness difference (ΔL*), chroma difference (ΔC*), and hue difference (Δh*)) were calculated using CMC (2:1) equation. The instrumental settings used were: 10° observer, D65 illuminant, specular reflectance included and aperture size 30mm. After folding each fabric twice, four readings were taken at different places on the fabric and averaged.

Washing fastness and crocking fastness

Washing fastness was measured according to AATCC Evaluation Procedure 7. For this a piece of dyed fabric was washed with a piece of multi-fiber strip. The rating on grey scale ranges are between 1 (poor) to 5 (excellent).

Crocking fastness of dyed fabric was evaluated by using a Crockmeter according to AATCC Test Method 8-2001. It measures the degree of color transfer from dyed fabric to white fabric both in wet and dry conditions. Range of values from 1 to 5 is rated as poor to excellent on grey scale.

Color strength (k/S) value

Color strength (K/S) or shade of dyed fabrics was calculated by using Kubelka Monk equation as follows:

$$K/S = (1-R)^2/2R \quad (i)$$

Where R= Reflectance percentage, K =Absorption co-efficient, and s=scattering co-efficient of dyes. The high K/S value of dyed fabric depicts deeper shade i.e. more the dyestuff in the fabric.

Results and Discussion

Effect of Fenton Oxidation on color removal

At acidic pH (3), Fenton process yielded a significant reduction of color (88-97%) in only 30 minutes of reaction time. By using optimum dose of Fenton reagent, wash-off of blue dyes exhibited highest color removal as shown in Fig. 2. It was investigated that comparatively less rate of decolorization was observed for red and orange dyes by Fenton oxidation. On the whole, Fenton treatment of wastewater was proved effective and this treated wastewater was used in wash-off step of dyeing.

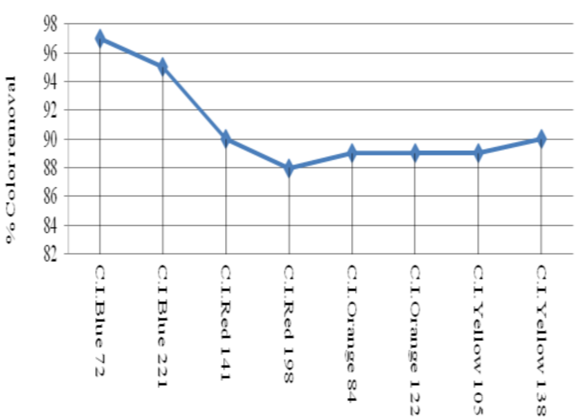


Fig. 2: Decolorization efficiency of Fenton oxidation at optimum conditions.

Color difference measurement

Color difference values of dyed fabric between reference (dyed in fresh water) and batch (using Fenton treated wash-off) samples were compared in terms of ΔL*(lightness/darkness), Δc*(weaker/stronger),Δh*(hue difference) and ΔE*cmc (total color difference) results are shown in Table 4.The commercially acceptable value for ΔE*cmc ≤ 1 is regarded as pass in textile industry . If the ΔL* value is positive, it means color of the batch sample is lighter than color of the reference, if the value is negative then it means the batch sample is darker than the reference. For C.I. Blue 72 batch sample achieved negligible total color difference ΔE* =0.96, lightness ΔL*=-2.16 and chroma Δc*=-0.39.The batch sample is greener Δa*=-0.05 and yellower Δb*=0.82.In case of C.I Blue 221 value of ΔE*cmc was equal to 0.31 and sample was approved in quality. The value of ΔL*=0.05 indicated lighter shade of batch sample. Δa*=-0.33 depicts greener shade and Δb*=0.29 yellower shade of batch sample. C.I. Red 141 showed acceptable results where ΔE* =0.86, ΔL* =-1.23 and Δ c*=-1.53. . In case of C.I Red 198 value of ΔE*cmc is equal to 0.59 and sample is regarded as pass. The value of ΔL*=0.49 indicated lighter shade of batch sample. Its Δa*=-0.10 depicts greener shade and Δb*=-0.49 bluer sample shade. For C.I. Orange 84 total color difference was slightly higher than standard value. ΔE*=1.17 indicated that batch sample is fail in quality. Color is slightly darker ΔL*=-0.95 and brighter Δ c*=1.83.For C.I Orange 122 value of total color difference was 1.16. ΔL* value of this sample was 1.32 represents darker shade and Δ c*=2.83 brighter than standard. In case of C.I. Yellow 105, ΔE*=2.17 which was considered fail in testing. Values of ΔL*=-4.52 and Δ c*=-3.38 were also very high for batch sample. C.I yellow 138 showed pass result with ΔE* =0.72.Color is slightly darker ΔL*=-1.03 and slightly brighter Δ c*=1.65.In short, Fenton treated wash-off proved capable of giving tolerable color difference values for batch dyeing.

Table-4: CIELAB Color difference values of standard and samples dyed in Fenton treated wastewater.

Dyes	CIELAB Color difference values					
	ΔL*	Δ a*	Δb*	Δ c*	Δh*	ΔE*cmc
C.I.Blue 72	-2.16	-0.05	0.82	-0.39	-0.72	0.96
C.I.Blue.221	0.05	-0.33	0.29	-0.31	-0.31	0.31
C.I.Red 141	-1.23	-1.53	0.32	-1.53	0.32	0.86
C.I.Red 198	0.49	0.10	-0.94	0.0	-0.94	0.59
C.I.Orange 84	-0.95	0.33	2.17	1.83	1.20	1.17
C.I.Orange 122	-1.38	1.64	2.36	2.83	0.48	1.16
C.I.Yellow 105	-4.52	1.26	-3.55	-3.38	-1.67	2.17
C.I.Yellow 138	-1.03	1.06	1.30	1.65	-0.32	0.72

Wash Fastness and Crocking Properties

The evaluation of color fastness to washing and crocking of dyed fabrics under investigation were summarized in Table 5. For the C.I. Reactive Blue 72 and C.I. Reactive Blue 221, color staining on un-mercerized cotton of multi- fiber strip was found to be 4-5 for both reference and batch, showing no change in washing fastness properties. In case of C.I Reactive Red 141, staining value for un-mercerized cotton was 5 for reference while for batch it was 4.5 which show negligible difference in wash fastness properties. In case of C.I. Reactive Orange 122 and C.I. Reactive Orange 84, both reference and batch exhibited comparable values, indicating identical fastness properties. Fastness properties of C.I. Reactive Yellow 105 and C.I. Reactive Yellow 138 were found almost identical to that of reference shade. Staining on Cellulose acetate of both reference and samples were found comparable.

Fabrics tested by dry and wet conditions of crocking fastness showed similar results in the range of 3 to 5 except C.I. Reactive Red 141 and C.I. Reactive Red 198. These dyes showed low values (2-2.3) poor on scale but same values for reference and batch dyed fabrics represents that Fenton treated wash-off water seemed fit to remove unfixed dyes efficiently. Overall results pertaining to wash fastness and wet and dry crocking concluded that commercially acceptable fastness properties were achieved with Fenton treated spent wash-off liquor, and no major deterioration of the color fastness to washing occurred over use of this method.

Table-5: Wash fastness and crocking properties of dyed samples

Reactive dyes	Sample	Crocking		Multi-fiber staining					
		Dry	Wet	Cellulose Acetate	Un-Mercerised Cotton	Nylon 6,6	Polyester Terylene	Acrylic (Courtelle)	Wool Worsted
Reactive Blue 72	Reference	5	5	4.5	5	5	5	4.5	4
	Batch	4.5	5	4	5	5	5	4.5	4
Reactive Blue 221	Reference	4.5	4	4.5	5	5	5	4.5	4
	Batch	4.5	4	4	5	5	5	4.5	4
Reactive Red 141	Reference	4.5	2.3	4	5	5	4.5	5	4
	Batch	4.5	2.3	4	4.5	4.5	4.5	5	4
Reactive Red 198	Reference	4.5	2.3	4	5	5	5	4.5	3.5
	Batch	4.5	2	3.4	4.5	5	5	4.5	3
Reactive Orange 84	Reference	4.5	4	4	5	5	5	5	4.5
	Batch	4.5	4	4	5	5	5	5	4.5
Reactive Orange 122	Reference	4.5	3.4	4	5	5	5	5	4
	Batch	4.5	3.4	4	5	5	5	5	4
Reactive Yellow 105	Reference	4.5	3.5	4	5	5	5	5	4
	Batch	4.5	3	4	5	5	5	5	4
Reactive Yellow 138	Reference	4.5	3	4	5	5	5	4.5	3.5
	Batch	4.5	3	3	5	5	5	4	3.5

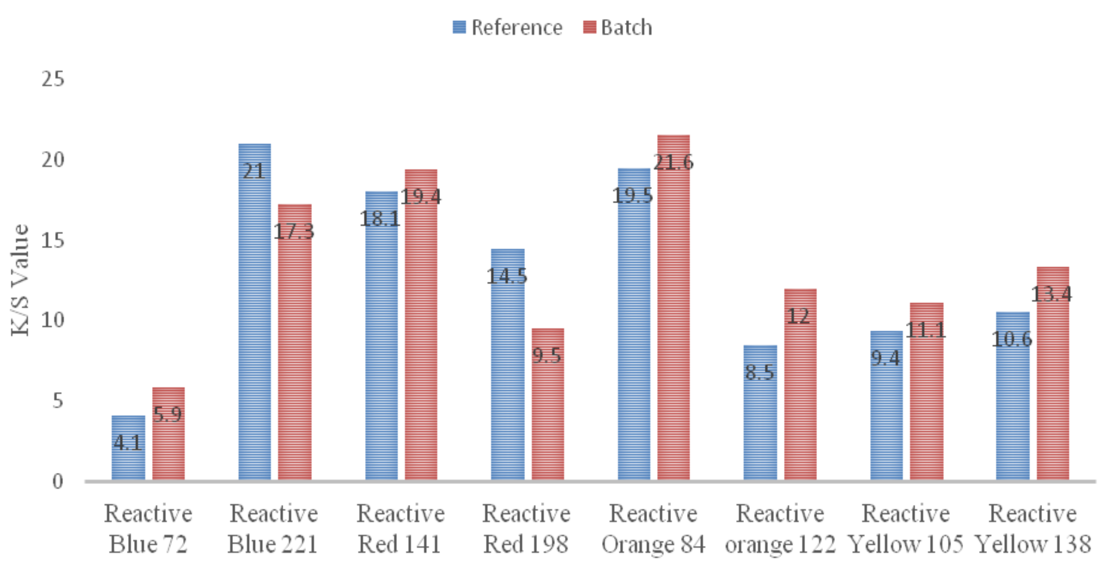


Fig. 3: Color strength (K/S) of dyed samples.

Color Strength (K/S) Measurements

Fig. 3 shows color strength (K/S) values of dyed samples washed conventionally and with Fenton treated wash-off wastewater. For reactive Blue 221 dye and reactive Red 198, graph shows that K/S value of batch is higher than reference which means reference is darker in color than batch. Reverse trend was observed for other dyes which means batch is darker than reference.

Conclusion

Fenton oxidation is an important technique in the field of wastewater treatment. This study evaluated a washing-off method with Fenton's reagent treated wastewater for removing unfixed hydrolyzed dyes on cotton fabrics during dyeing. Unfixed dyes were wash-off by application of Fenton treated wastewater to attain desired level of color and wash fastness. The competence of the Fenton method was assessed on cotton fabrics dyed with C.I. Reactive Blue 72, C.I. Reactive Blue 221, C.I. Reactive Red 141, C.I. Reactive Red 198, C.I. Reactive Orange 84, C.I. Reactive orange 122, C.I. Reactive Yellow 105 and C.I. Reactive Yellow138 in deep shades. Based on the results achieved in this study, it is concluded that Fenton based washing-off method is proficient to generate similar color and wash fastness properties with least color difference and helpful in water conservation by wastewater recycling. It is suggested that the effect of Fenton on fabrics dyed with reactive dyes should be extensively evaluated on pilot scale experimentation to assess the suitability of the method on commercial scale.

References

1. R. Żyłła, K. Michalska, L. Kos and S. Ledakowicz, Effect of UV/H_2O_2 on Fouling in Textile Wastewater Nanofiltration, *Fibres Text. East. Eur*., **1**, 99 (2012).
2. S. M. Burkinshaw and O. Kabambe, Attempts to reduce water and chemical usage in the removal of reactive dyes: Part 1 bis (aminochlorotriazine) dyes, Dyes. *Pigm*., **83**, 363 (2009).
3. I. Ciabatti, F. Tognotti and L. Lombardi, Treatment and reuse of dyeing effluents by potassium ferrate, *Desalin*., **250**, 222 (2010).
4. A. Moussa, A. El Ghali, S. Ellouzi and F. Sakli.). Colour and fastness study of wool dyeing in multiple reuse dye baths using acid and reactive dyestuffs in laboratory scale. *J. Text. Inst*., **104**, 260 (2013).
5. A. Mittal, J.Mittal, A.Malviya and V. K. Gupta, Removal and recovery of Chrysoidine Y from aqueous solutions by waste materials. *J. Colloid. Interfec. Sci*., **344**, 497, (2010).
6. R. Saravanan,V. K. Gupta, E.Mosquera and F. Gracia, Preparation and characterization of V_2O_5/ZnO nanocomposite system for photocatalytic application. *J. Mol. Liq.*, **198**, 409, (2014).
7. V. K. Gupta, R. Jain, A. Nayak, S. Agarwal and M. Shrivastava, Removal of the hazardous dye tartrazine by photodegradation on titanium dioxide surface. *Mater. Sci. Eng*., **31**, 1062 (2011).
8. R. Saravanan, S. Karthikeyan, V. K. Gupta, G. Sekaran, V. Narayanan and A. Stephen, Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination. *Mater Sci. Eng*, **33**, 91, (2013).
9. M. Ghaedi, S. Hajjati, Z. Mahmudi, I. Tyagi, S. Agarwal, A. Maity and V. K. Gupta, Modeling of competitive ultrasonic assisted removal of the dyes–Methylene blue and Safranin-O using Fe_3O_4 nanoparticles. *Chem. Eng. J.*, **268**, 28 (2015).
10. M. S. U. Rehman, S. Mehmood, A. Ahmad, A. Saeed and T. Mahmood, Color and COD reduction of biotreated complex wastewater using ozonation process. *J. Pak. Inst. Chem. Eng*., **39**, 81, (2011).
11. S. Karthikeyan, C. Anandan, J.Subramanian and G. Sekaran, Characterization of iron impregnated polyacrylamide catalyst and its application to the treatment of municipal wastewater. *RSC Adv*., **3**, 15044 (2013).
12. Y. Sindhi and M. Mehta, COD removal of different industrial wastewater by fenton oxidation process, *J. Eng. Sci. Res. Tech.*, **3**, 1134 (2014).
13. O. Gokkus, F. Coskun, M. Kocaoglu and Y. S. Yldz, Determination of optimum conditions for color and COD removal of Reactive Blue 19 by Fenton oxidation process. *Desalin. Water Treat.*, **52**, 6156 (2014).
14. A. F. Bertea, R. Butnaru and R. A. Z. V. A. N. Berariu, Reducing pollution in reactive cotton dyeing through wastewater recycling, *Cellul. Chem. Technol*., **47**,133 (2013).
15. A. Mangat, I. A. Shaikh, F. Ahmed, S. Munir and M.Baqar, Fenton oxidation treatment of spent wash-off liquor for reuse in reactive dyeing, *Tech.J.Univ. Eng.Technol. (UET) Taxila*, **19**, 43 (2014).
16. I. A. Shaikh, N. Ahmad and F. Urooj, A novel method to improve color fastness of deep shade reactive dyeing using ozone in washing off, *AATCC rev*., **10**, 73(2010).

17. X. Lu, L. Liu, R. Liu and J. Chen, Textile wastewater reuse as an alternative water source for dyeing and finishing processes: A case study, *Desali*., **258**, 229 (2010).
18. T. A.Saleh, and V. K. Gupta, Photo-catalyzed degradation of hazardous dye methyl orange by use of a composite catalyst consisting of multi-walled carbon nanotubes and titanium dioxide. *J. Colloid. Interface Sci*., **371**, 101 (2012).
19. E. K. Aziz, R. Abdelmajid, L. M. Rachid and E. H. Mohammadine, Adsorptive removal of anionic dye from aqueous solutions using powdered and calcined vegetables wastes as low-cost adsorbent. *Arab J. Basic Appl.Sci*., **25**, 93 (2018).
20. J. Zhang, Q. Zhou and L. Ou, Kinetic, isotherm, and thermodynamic studies of the adsorption of methyl orange from aqueous solution by chitosan/alumina composite. *J. Chem. Eng.Data*, **57**, 412, (2011).
21. O. S. Bello and M. A. Ahmad, Coconut (Cocos nucifera) shell based activated carbon for the removal of malachite green dye from aqueous solutions. *Sep. Sci. Technol*., **47**, 903 (2012).
22. C. Ozer, M. Imamoglu, Y.Turhan and F. Boysan, Removal of methylene blue from aqueous solutions using phosphoric acid activated carbon produced from hazelnut husks. *Toxicol. Environ.Chem*., **94**, 1283, (2012).
23. B. Royer, N. F. Cardoso, E. C. Lima, J. C. Vaghetti, N. M. Simon, T. Calvete and R. C. Veses, Applications of Brazilian pine-fruit shell in natural and carbonized forms as adsorbents to removal of methylene blue from aqueous solutions Kinetic and equilibrium study. *J. Hazard Mater*., **164**, 1213, (2009).
24. M. Valix, W. H. Cheung and G. Mckay, Preparation of activated carbon using low temperature carbonisation and physical activation of high ash raw bagasse for acid dye adsorption. *Chemos*., **56**, 493, (2004).
25. V. Gunasekar and V. Ponnusami, Kinetics, equilibrium, and thermodynamic studies on adsorption of methylene blue by carbonized plant leaf powder. *J.chem*., **2013**,6 (2013).
26. M. M. Mohamed, Acid dye removal: comparison of surfactant-modified mesoporous FSM-16 with activated carbon derived from rice husk. *J. Colloid. Interface Sci*., **272**, 28, (2004).
27. J. Yang and K. Qiu, Preparation of activated carbons from walnut shells via vacuum chemical activation and their application for methylene blue removal. *Chem. Eng.J*. **165**, 209 (2010).
28. Y. Fu and T. Viraraghavan, Dye biosorption sites in *Aspergillus niger*. *Bioresour. Technol*., **82**, 139, (2002).
29. I. A. W. Tan, A. L. Ahmad and B. H. Hameed, Adsorption of basic dye using activated carbon prepared from oil palm shell: batch and fixed bed studies. *Desalin*., **225**, 13, (2008).
30. Y. Fu and T. Viraraghavan, Removal of Congo Red from an aqueous solution by fungus *Aspergillus Niger*. *Adv. Environ.Res*., **7**, 239, (2002).
31. R. Malarvizhi and Y. S. Ho, The influence of pH and the structure of the dye molecules on adsorption isotherm modeling using activated carbon. *Desalin*., **264**, 97, (2010).
32. Y. S. Ho, T. H. Chiang and Y. M. Hsueh, Removal of basic dye from aqueous solution using tree fern as a biosorbent. *Process Biochem*., **40**, 119,(2005).
33. M. Özacar and İ. A. Şengil, Adsorption of metal complex dyes from aqueous solutions by pine sawdust. *Bioresour.technol*., **96**, 791, (2005).
34. Z. Aksu and S. Tezer, Biosorption of reactive dyes on the green alga Chlorella vulgaris. *Process Biochem*., **40**, 1347,(2005).
35. M. Ş. Tanyildizi, Modeling of adsorption isotherms and kinetics of reactive dye from aqueous solution by peanut hull. *Chem.Eng. J*., **168**, 1234. (2011).