



## Decolorization of textile wastewater by gamma irradiation and its reuse in dyeing process

M.A. Rahman Bhuiyan<sup>a,b,\*</sup>, M. Mizanur Rahman<sup>a</sup>, Abu Shaid<sup>b</sup>, M.A. Khan<sup>c</sup>

<sup>a</sup>Department of Applied Chemistry and Chemical Engineering, University of Dhaka, Dhaka 1000, Bangladesh, Tel. +88029204712; Email: arahman@duet.ac.bd

<sup>b</sup>Department of Textile Engineering, Dhaka University of Engineering & Technology, DUET, Gazipur 1700, Bangladesh

<sup>c</sup>Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission, P.O. 3787, Dhaka-1000, Bangladesh

Received 8 November 2013; Accepted 28 February 2014

### ABSTRACT

This paper describes the scope of employing high-energy gamma irradiation for textile wastewater treatment and the possibility of using the treated wastewater in the dyeing of knitted cotton fabric. The treatment was carried out in Cobalt-60 gamma radiation source at different irradiation doses (3, 5, 8, and 12 kGy). Then, the irradiated wastewater was used for dyeing of cotton fabric with reactive dye. The performance of the fabric dyed with treated wastewater was compared to that of the fabric dyed with freshwater. Hence, the dyeing performance was evaluated by comparing the depth of shades of both types of dyed fabrics from the analysis of absorption spectrum ( $K/S$  value vs. wavelength). The absorption curves of irradiated wastewater dyed fabric in light, medium, and dark shade of three different colors have shown close match to their corresponding freshwater dyed fabric. Variation of shade between the dyed fabrics, representing by  $\Delta E$  values, were also found within the maximum acceptable limit as it ranges from 0.02 to 0.9. The color fastness of the dyed fabric was also measured with respect to perspiration, rubbing, and washing. In case of fastness, both types of fabrics have shown similar rating (4–5) which lies between “good” to “excellent”.

*Keywords:* Textile wastewater; Gamma irradiation; Decoloration; Cotton fabric; Dyeing

### 1. Introduction

Textile industries have great significance in terms of economic contribution as well as employment generation in Bangladesh. But this sector is the major source of environmental pollution. Huge amount of water is consumed in several stages to get finished products in a textile processing plant. The wastewater generated in textile processing plants is contaminated with toxic synthetic colorants and various

perilous chemicals. Water is used as medium for the processing of textile materials. Nearly, 70–150 l of water is required for the processing of 1 kg cotton fabric [1]. Again among the textile fibers, about 48% of cotton fibers are consumed as clothing material all over the globe [2,3] and 20% of those are dyed with reactive dyes [3]. Knit dyeing industries have grown rapidly in Bangladesh, where reactive dyes are used extensively. They are water-soluble anionic dyes exhibiting one or more functional group capable of forming covalent bond with cellulose and are not

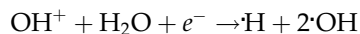
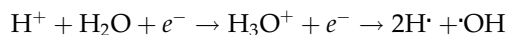
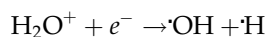
\*Corresponding author.

suitable for recycling [4]. A considerable amount (10–40%) of unfixed hydrolyzed dyes remains in textile wastewater causing highly colored effluent discharge [5]. Thus, the reactive dye is the main source of pollution in the textile industry. Moreover, rivers, canals, and streams of Bangladesh are extensively contaminated with textile wastewater due to the direct discharge of effluent by the industries. As a result, textile industries in Bangladesh are creating agonizing problems by polluting the existing water bodies and depleting the groundwater level. These conditions will make the life unsafe and will not support the sustainable development of textile industries in Bangladesh. Likewise, due to increasing population, the industries have to face the pressure to recover and reuse some of its wastewater, or face the danger of being shutdown [6]. This is due to the combined pressure of increasing water demand and wastewater treatment costs. As a result, the reuse of wastewater has drawn a great attention to the researchers around the globe [7–11].

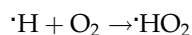
The color of the textile wastewater is not removed efficiently by ordinary treatment technology. Typical techniques for treatment of wastewater include the classical methods such as adsorption [12–14], coagulation [15,16], filtration [17], and sedimentation [18]. All these techniques have some degree of effectiveness, but all of them generate secondary waste which needs to be tackled further [19]. On the contrary, biological treatment based on activated sludge can efficiently reduce the COD, but complete color removal is not possible with this technique [20]. Moreover, huge space is required to set up a biological plant. In addition, applications of membrane technologies in textile industries are not very common yet [20]. Again, the ultra-filtration techniques prove its success mainly for the recovery of size materials from desizing effluent and indigo dye particles from the discharged dye liquor [21].

In this regard, ionization radiation technology is the promising technique to decolorize and decompose the textile wastewater [22] with no further generation of secondary waste. The radiation technology methods normally utilize a strong oxidizing species such as  $\cdot\text{OH}$  radicals which have high electrochemical oxidation potential and cause a sequence of reactions thereafter to breakdown the macromolecules of dye into smaller and less harmful substances [23]. High-energy radiation produces instantaneous radiolytic transformation through energy transfer from high-energy accelerated electrons to the orbital electrons of water molecules. Absorbed energy disturbs the electron system of the molecule resulting in the

breakage of interatomic bonds and ionizing the water molecules forming  $\text{H}_2\text{O}^+$ . Various active species are generated due to the radiation interaction between gamma rays and water as shown in the equations given below.



In the presence of dissolved air or oxygen, a radical known as perhydroxyl radical i.e.  $\text{HO}_2$  is also formed:



Generally, these species are hydroxyl radical ( $\cdot\text{OH}$ ), hydrogen radical ( $\text{H}\cdot$ ), hydrated electron ( $e^-_{\text{aq}}$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and so on [24]. Among these products, the most reactive species are hydroxyl radical and hydrated electron. Hydroxyl radical attacks the conjugated double bond of the dye particle and breaks it [24]. Thus, the colored dye molecules produce colorless smaller molecules, which results in the decoloration of the effluent.

This study explores the feasibility of reusing textile wastewater for the dyeing cotton fabric after decolorizing by gamma irradiation, which will eventually reduce the wastewater generation and freshwater consumption rate.

## 2. Materials and methods

### 2.1. Sample collection and irradiation

Textile wastewater was collected directly from the equalization basin of Effluent Treatment Plant of Divine Textiles Mills Ltd, Gazipur, Bangladesh. Collected water samples were irradiated in a 500 ml plastic bottle at four different radiation doses (3, 5, 8, and 12 kGy) at room temperature at a dose rate 13 kGy/h without any further treatment or dilution. The electromagnetic radiation (gamma rays) emitted from Cobalt-60 source was carried out at Institute of Radiation and Polymer Technology, Bangladesh Atomic Energy Commission, Dhaka. Then, the presence of color and pH value in wastewater was measured by UV spectrophotometer and digital pH meter, respectively. At last, the irradiated wastewaters were filtered to remove any coarse materials before using for dyeing performance analysis.

## 2.2. Measurement of pH

The pH of the raw wastewater and irradiated samples was measured directly by digital pH meter (Eco-scan, 1161795) from Eutech Instruments, Singapore.

## 2.3. Measurement of color removal efficiency

The color absorbance of raw and irradiated wastewater was measured by UV–Vis spectrophotometer (T60, PG Instrument from UK). The degree of decoloration was then calculated from the decrease in absorbance at maximum absorption wavelength after irradiation as follows [19]:

$$\text{Decoloration (\%)} = \frac{A_0 - A_1}{A_0} \times 100 \quad (1)$$

where  $A_0$  and  $A_1$  are the maximum absorbance in visible area of the textile wastewater before and after irradiation.

## 2.4. Dyeing of fabric samples

Three commercial reactive dyes namely Novacron Yellow FN2R, Novacron Red FN2BL, and Novacron Blue FNR were used to dye 5 g scoured, bleached, and enzyme-treated 100% cotton plain knit fabric (120 GSM) in a laboratory dyeing machine. Dyestuffs were collected from Swiss Colours Ltd. Bangladesh and commercial detergent (Imeron PCLF) and leveling agent (Drimagen E3R) were collected from Clarant, Bangladesh and used as received. Sodium sulfate (Glauber salt), soda ash, and acetic acid were used as received and all were of commercial grade. The dyeing was carried out in Sandolab Infrared lab dyeing machine from Copower Technology Ltd., Taiwan.

Fabric samples were dyed with each of the above-mentioned dyes at three different shade percentages (5, 1.5, and 0.5% on the weight of fabric) using fresh and irradiated wastewater. General recipe is given in Table 1.

Fabric samples of 5.0 g ( $\pm 5\%$ ) were dyed for each color in three different shades by exhaust dyeing method. The dyeing procedure is shown in Fig. 1.

## 2.5. Dyeing performance test

The performance of dyed fabric regarding the depth of color was analyzed using spectrophotometer (Data Color 650 from USA). Color fastness to wash, rubbing, and perspiration was measured according to ISO 105 C03, ISO 105 X 12: 1993, and ISO 105 E04, respectively. Wash fastness tester (Gyrowash model no: 415/8), perspiration fastness tester (Perspirometer model: HX-30), and rubbing fastness tester (Crockmeter, model no: 670) from James H. Heal & Co, UK were used for the respective fastness testing.

## 3. Results and discussions

### 3.1. Analysis of pH change

The actual pH of the reactive dye bath normally lies between 10 and 11. However, the final pH of the wastewater in mixing tank, wastewaters from dyebath mixed with other wastewater from other processes, has been found to be around 8–9. After irradiation, the pH value of the wastewater was decreased from 9 to nearly neutral value of 7–7.5 due to the formation of organic acids (such as dicarboxylic acids or monocarboxylic acids like acetic acid and other acidic aromatic compounds or carboxylic acid) due to the breakdown of aromatic rings [23]. The reduction percentage of pH of wastewater after irradiation is shown in Fig. 2.

Table 1  
General dyeing recipe for all test samples

| Shade % →             | Deep shade (5%) | Medium shade (1.5%) | Light shade (0.5%) |
|-----------------------|-----------------|---------------------|--------------------|
| <i>Ingredients ↓</i>  |                 |                     |                    |
| Wetting agent         | 1 g/l           | 1 g/l               | 1 g/l              |
| Leveling agent        | 1 g/l           | 1 g/l               | 1 g/l              |
| Dyes                  | 5.0% (owf)      | 1.5% (owf)          | 0.5% (owf)         |
| Glauber salt          | 40 g/l          | 30 g/l              | 15 g/l             |
| Soda ash              | 10 g/l          | 8 g/l               | 4 g/l              |
| Material liquor ratio | 1:10            | 1:10                | 1:10               |

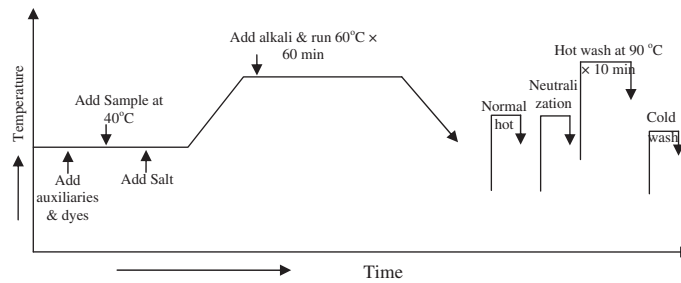


Fig. 1. Dyeing curve of cotton fabric with reactive dye.

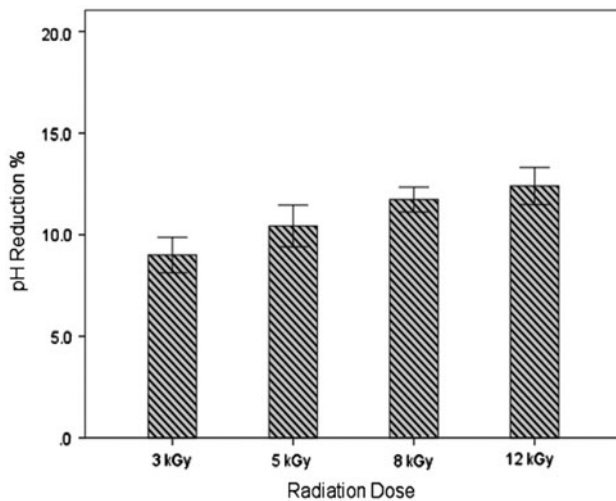


Fig. 2. pH reduction percentages of irradiated wastewater at different radiation doses.

From the study, it has been found that, though the pH of the final wastewater of a textile industry may vary depending on the nature of processing but after irradiation the pH has decreased with the radiation doses but the rate of reduction is not significant with increasing radiation dose. The insignificant reduction of pH of wastewater with higher radiation dose is due to the organic acid resulted from the breakdown of benzene ring, is converted to further smaller components [23].

### 3.2. Analysis of color removal efficiency

Color removal efficiency was analyzed by measuring the presence of color in irradiated and unirradiated wastewater through UV–Vis spectrophotometer. However, color of the textile wastewater differs significantly according to different textile processing, chemicals, and dyes. As a result, a fixed radiation dose

cannot be suggested for all type of textile wastewater. The current research applied 3, 5, 8, and 12 kGy radiation dose on various types of textile wastewater, which were collected from time to time throughout the year. Then, the color reduction percentages were measured. The color reduction percentages of collected wastewater at above-mentioned four radiation doses are given in Fig. 3.

From the figure, it is clear that color reduction percentages increase according to the gradual increment of radiation dose. The statistical analysis shows that there are fluctuations in color reduction at different radiation doses resulting in longer error bar due to different types of dye present in wastewater. The amount of color reduction by radiation depends on color and structure [22] of the dye. Wastewater collected for the current investigation was not taken selectively. Therefore, water samples were of different types containing different amount of dyestuff that shows variation in the reduction of color by irradiation. Furthermore, from the investigation, it has also been found that color reduction percentages do not increase significantly after the increment of radiation dose beyond 5 kGy. So, considering the cost effectiveness of the process, only 5 kGy irradiated wastewater was selected for the current research purpose to analyze the dyeing performance.

### 3.3. Shade matching

In a commercial dye house, textile materials are dyed to match the color of a produced shade against a given standard. This is known as shade matching. In case of shade matching, the variation of shade is determined using spectrophotometer and the term is expressed in CMC  $\Delta E$  value [3].

$$\Delta E_{\text{CMC}} = \sqrt{\left(\frac{\Delta L^*}{l \times S_L}\right)^2 + \left(\frac{\Delta C^* ab}{c \times S_C}\right)^2 + \left(\frac{\Delta H^* ab}{S_H}\right)^2} \quad (2)$$

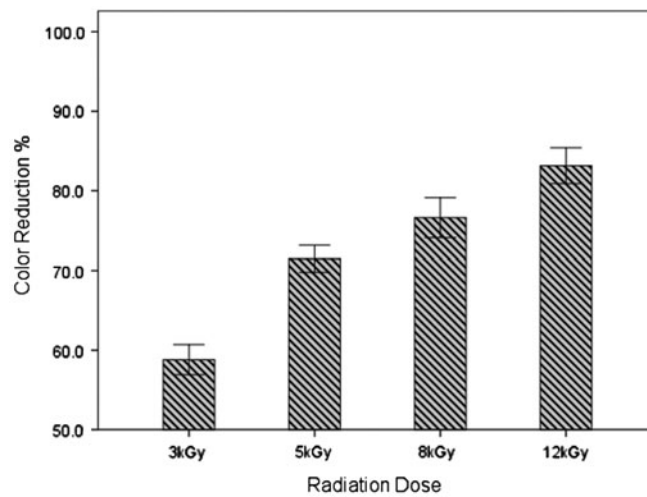


Fig. 3. Amount of color reduction of wastewater at different radiation doses.

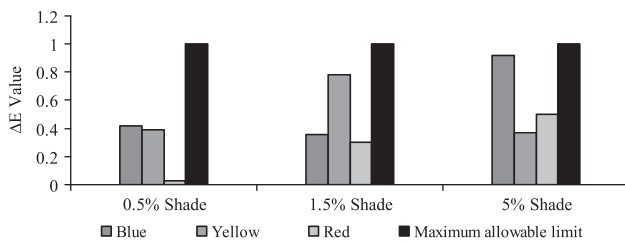


Fig. 4. Color difference ( $\Delta E$  values) of wastewater treated fabrics and freshwater treated fabrics at different shade percentages with respect to maximum allowable limit.

where  $\Delta L^*$ ,  $\Delta C^*ab$ ,  $\Delta H^*ab$ ,  $l$ ,  $S_L$ ,  $S_C$ ,  $c$ , and  $S_H$  signify their respective values as discussed by Broadbent [3]. The maximum acceptable value for  $\Delta E$  is 1 [3], where

lower value indicates that the reproduced color is closer to the original and vice versa. In the present study, the fabric samples were dyed in three different shades in three different shade percentages from light to dark. The  $\Delta E$  values were measured in respect to freshwater samples that are shown in Fig. 4.

Fig. 4 illustrates that all the  $\Delta E$  values lies under the maximum allowable limit, which signify that dyeing with irradiated wastewater does not pose any problem in shade matching. The lower  $\Delta E$  values also denote that the dye exhaustion and fixation were almost similar in both cases of dyeing with freshwater and wastewater. Hence, it can be concluded that the irradiated wastewater has no negative influence for dyeing and color reproduction of fabrics.

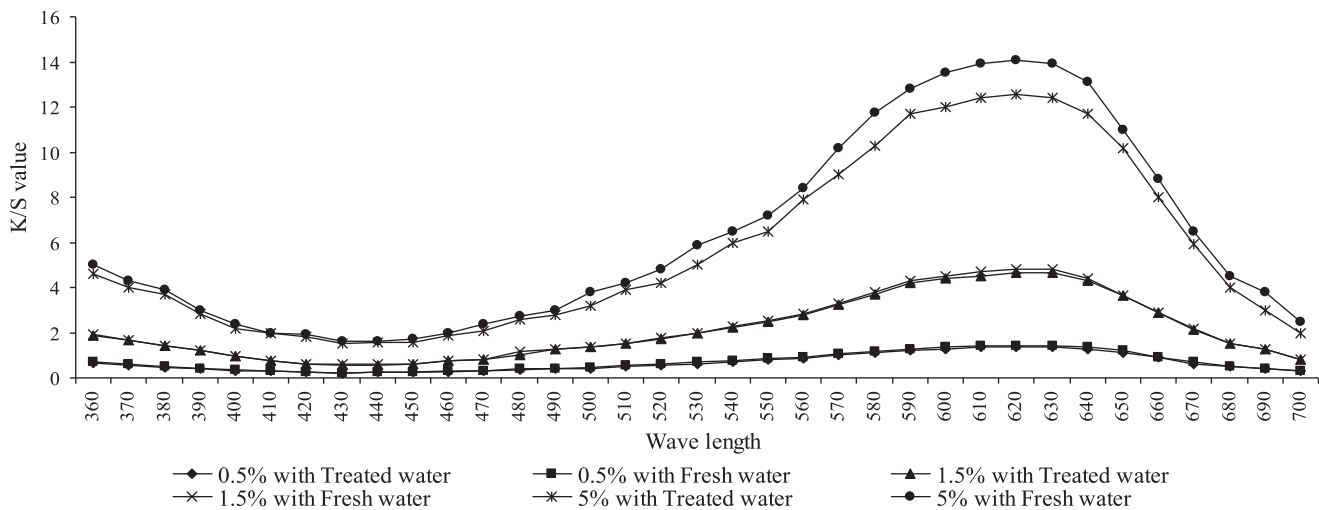


Fig. 5. Dye absorption (K/S value vs. wavelength) at  $\lambda_{max} = 630$  nm of Novacron Blue FNR.

### 3.4. Color depth analysis

Color depth of the dyed fabrics was analyzed by measuring the  $K/S$  values of respective shades. Color measuring instrument (spectrophotometer) determines the  $K/S$  value of a given fabric through Kubelka–Munk equation as follows [3].

$$\frac{K}{S} = \frac{(1 - R)^2}{2R} \quad (3)$$

where  $R$  = reflectance percentage,  $K$  = absorption co-efficient, and  $S$  = scattering co-efficient of dyes. This value was derived from the attenuation ratio of light due to absorption and scattering, which was found to

be based on reflectance. The values found for all the fabrics of different color and depth of shade are shown in Figs. 5–7.

The figures for each color shows six different curves for three different shade percentages. The more the dyestuff in the fabric causes the deeper shade, resulting in higher  $K/S$  value in the curve. The curves formed by the 5% shade shows elevated  $K/S$  value, whereas the curves for 0.5% shade forms almost flattened curves due to lower  $K/S$  value. However, the fabrics dyed in fresh and treated water shows nearly similar curves for a particular shade percentage of each color. This indicates that the fabric absorbed the same amount of dyestuff from both types of dyebath (fresh and treated water). Because the absorption of

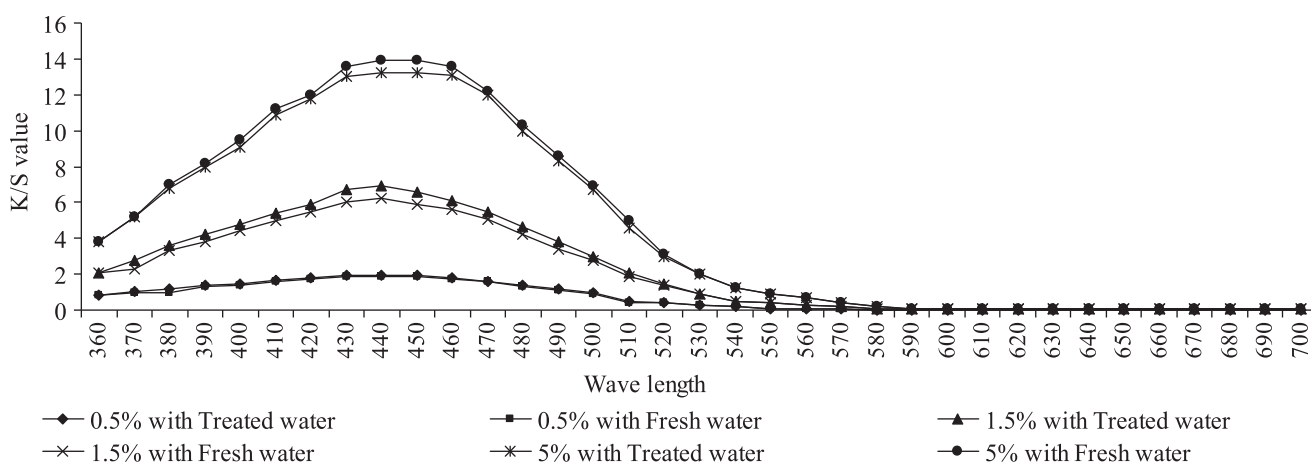


Fig. 6. Dye absorption ( $K/S$  value vs. wavelength) at  $\lambda_{\text{max}} = 440$  nm of Novacron Yellow FN2R.

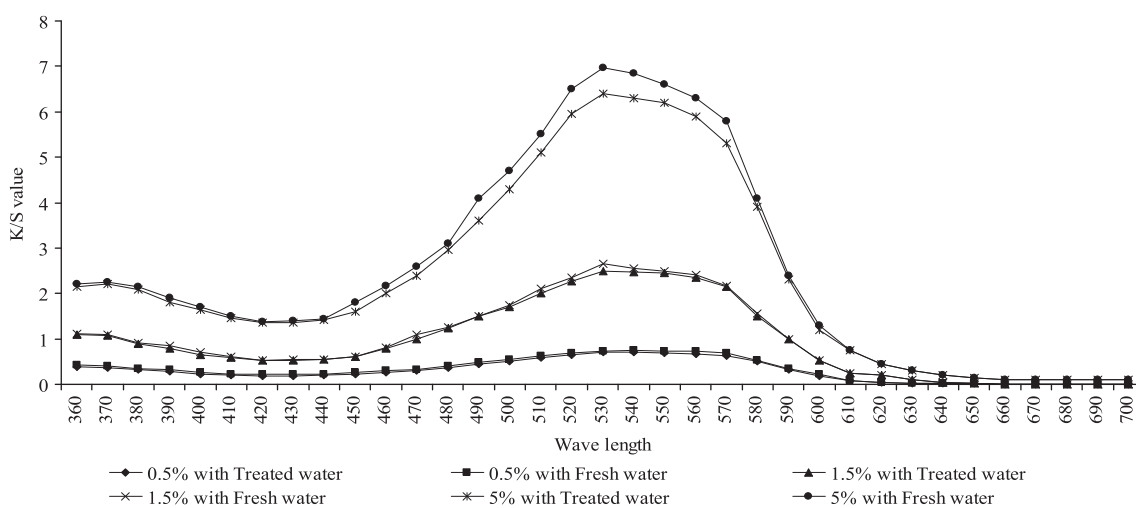


Fig. 7. Dye absorption ( $K/S$  value vs. wavelength) at  $\lambda_{\text{max}} = 540$  nm of Novacron Red FN2BL.



the same amount of dyes, the depth of shades was also found almost similar in the freshwater dyed samples and irradiated wastewater dyed samples.

### 3.5. Color fastness properties of the dyed fabrics

Three types of color fastnesses such as color fastness to rubbing, washing, and perspiration of the dyed fabrics were measured by gray scale. Color

fastness to washing and perspiration was assessed by color change options with respect to medium cellulosic wash. Rubbing fastness of dyed fabric samples was evaluated both in dry and wet condition. The color fastness ratings of freshwater and treated water dyed fabrics are tabulated in the Tables 2–4.

All the fabric samples are dyed in similar dyeing conditions except water (fresh and treated) which is used as dyeing medium. In the previous section,

Table 2  
Color fastness to rubbing (dry and wet) of dyed cotton fabric

| Dye                  | Shade (%) | Fresh water dyed |     | Treated water dyed |     |
|----------------------|-----------|------------------|-----|--------------------|-----|
|                      |           | Dry              | Wet | Dry                | Wet |
| Novacron Yellow FN2R | 0.5       | 4/5              | 4/5 | 4/5                | 4/5 |
|                      | 1.5       | 4/5              | 4/5 | 4/5                | 4/5 |
|                      | 5.0       | 4                | 3/4 | 4                  | 3/4 |
| Novacron Red FN 2BL  | 0.5       | 4/5              | 4/5 | 4/5                | 4/5 |
|                      | 1.5       | 4/5              | 4/5 | 4/5                | 4/5 |
|                      | 5.0       | 4                | 4   | 4                  | 3/4 |
| Novacron Blue FNR    | 0.5       | 4/5              | 4/5 | 4/5                | 4/5 |
|                      | 1.5       | 4/5              | 4   | 4/5                | 4   |
|                      | 5.0       | 4                | 3/4 | 4                  | 3/4 |

Table 3  
Color fastness to washing (color change) of dyed cotton fabric

| Dye                  | Shade (%) | Freshwater dyed | Treated water dyed |
|----------------------|-----------|-----------------|--------------------|
| Novacron Yellow FN2R | 0.5       | 4               | 4                  |
|                      | 1.5       | 4/5             | 4/5                |
|                      | 5.0       | 4/5             | 4/5                |
| Novacron Red FN 2BL  | 0.5       | 4/5             | 4/5                |
|                      | 1.5       | 4/5             | 4/5                |
|                      | 5.0       | 4/5             | 4                  |
| Novacron Blue FNR    | 0.5       | 4               | 4/5                |
|                      | 1.5       | 4               | 4                  |
|                      | 5.0       | 4               | 4                  |

Table 4  
Color fastness to perspiration (color change) of dyed cotton fabric

| Shade                | Shade (%) | Freshwater dyed | Treated water dyed |
|----------------------|-----------|-----------------|--------------------|
| Novacron Yellow FN2R | 0.5       | 4               | 4                  |
|                      | 1.5       | 4/5             | 4/5                |
|                      | 5.0       | 4/5             | 4/5                |
| Novacron Red FN 2BL  | 0.5       | 4/5             | 4/5                |
|                      | 1.5       | 4/5             | 4/5                |
|                      | 5.0       | 4/5             | 4/5                |
| Novacron Blue FNR    | 0.5       | 4               | 4/5                |
|                      | 1.5       | 4               | 4                  |
|                      | 5.0       | 4               | 4                  |

similarity of shade has been discussed. In view of similar depth of shade, it can be predicted that the dyed fabrics will also show similar color fastness properties. The results of all color fastness tests carried out for the current research have supported the prediction. The color fastness results in the tables show that fresh and treated water dyed fabrics have almost similar fastness rating of “good” to “excellent” (within numerical grade 4–5) [3] with very negligible variation.

#### 4. Conclusion

Dyeability of textile wastewater after gamma irradiation has been investigated. The detailed results have demonstrated that the dyeing performance of a fabric in respect to depth of shade, shade matching, and fastness rating is quite acceptable when the irradiated wastewater is used as dyeing medium instead of freshwater. So, it is concluded that irradiated wastewater can be used satisfactorily for the dyeing of textile materials.

#### References

- [1] C. Allègre, P. Moulin, M. Maisseu, F. Charbit, Treatment and reuse of reactive dyeing effluents, *J. Membr. Sci.* 269 (2006) 15–34.
- [2] M. Mahbulul Bashar, M. Khan, An overview on surface modification of cotton fiber for apparel use, *J. Polym. Environ.* 21 (2012) 181–190.
- [3] A.D. Broadbent, *Basic Principle of Textile Coloration*, Society of Dyers and Colorists, West Yorkshire, 2001.
- [4] A. Erswell, C.J. Brouckaert, C.A. Buckley, The reuse of reactive dye liquors using charged ultrafiltration membrane technology, *Desalination* 70 (1988) 157–167.
- [5] P. Cooper, Removing colour from dyehouse waste waters – A critical review of technology available, *J. Soc. Dyers Colour.* 109 (1993) 97–100.
- [6] C. Tang, V. Chen, Nanofiltration of textile wastewater for water reuse, *Desalination* 143 (2002) 11–20.
- [7] B. Van der Bruggen, B. Daems, D. Wilms, C. Vandecasteele, Mechanisms of retention and flux decline for the nanofiltration of dye baths from the textile industry, *Sep. Purif. Technol.* 22–23 (2001) 519–528.
- [8] I. Koyuncu, E. Kural, D. Topacik, Pilot scale nanofiltration membrane separation for waste management in textile industry, *Water Sci. Technol.* 43 (2001) 233–240.
- [9] S.N. Gaeta, U. Fedele, Recovery of water and auxiliary chemicals from effluents of textile dye houses, *Desalination* 83 (1991) 183–194.
- [10] G. Ciardelli, L. Corsi, M. Marcucci, Membrane separation for wastewater reuse in the textile industry, *Resour. Conserv. Recycl.* 31 (2001) 189–197.
- [11] I. Koyuncu, Influence of dyes, salts and auxiliary chemicals on the nanofiltration of reactive dye baths: Experimental observations and model verification, *Desalination* 154 (2003) 79–88.
- [12] E.N. El Qada, S.J. Allen, G. Walker, Adsorption of basic dyes from aqueous solution onto activated carbons, *Chem. Eng. J.* 135 (2008) 174–184.
- [13] B.H. Hameed, A.A. Ahmad, N. Aziz, Isotherms, kinetics and thermodynamics of acid dye adsorption on activated palm ash, *Chem. Eng. J.* 133 (2007) 195–203.
- [14] M.A. Rauf, I.A. Shehadi, W.W. Hassan, Studies on the removal of Neutral Red on sand from aqueous solution and its kinetic behavior, *Dyes Pigm.* 75 (2007) 723–726.
- [15] A.L. Ahmad, S.W. Puasa, Reactive dyes decolorization from an aqueous solution by combined coagulation/micellar-enhanced ultrafiltration process, *Chem. Eng. J.* 132 (2007) 257–265.
- [16] B. Shi, G. Li, D. Wang, C. Feng, H. Tang, Removal of direct dyes by coagulation: The performance of preformed polymeric aluminum species, *J. Hazard. Mater.* 143 (2007) 567–574.
- [17] J.H. Mo, Y.H. Lee, J. Kim, J.Y. Jeong, J. Jegal, Treatment of dye aqueous solutions using nanofiltration polyamide composite membranes for the dye wastewater reuse, *Dyes Pigm.* 76 (2008) 429–434.
- [18] A.N.M. Bagyo, H. Arai, T. Miyata, Radiation-induced decoloration and sedimentation of colloidal disperse dyes in water, *Appl. Radiat. Isot.* 48 (1997) 175–181.
- [19] M.A. Rauf, S.S. Ashraf, Radiation induced degradation of dyes – An overview, *J. Hazard. Mater.* 166 (2009) 6–16.
- [20] A. Bes-Piá, J.A. Mendoza-Roca, M.I. Alcaina-Miranda, A. Iborra-Clar, M.I. Iborra-Clar, Reuse of wastewater of the textile industry after its treatment with a combination of physico-chemical treatment and membrane technologies, *Desalination* 149 (2002) 169–174.
- [21] D. Şolpan, O. Güven, Decoloration and degradation of some textile dyes by gamma irradiation, *Radiat. Phys. Chem.* 65 (2002) 549–558.
- [22] N. Getoff, Radiation chemistry and the environment, *Radiat. Phys. Chem.* 54 (1999) 377–384.
- [23] A.N.M. Bagyo, W.A. Lindu, S. Sadjirun, E.K. Winarno, E. Widayat, H.W. Arayanti, Radiation Induced Degradation of Organic Pollutants in Wastewater, Center for the application of Isotopes and Radiation, Jakarta, 2001.
- [24] M.A. Rauf, S.B. Bukallah, A. Hamadi, A. Sulaiman, F. Hammadi, The effect of operational parameters on the photoinduced decoloration of dyes using a hybrid catalyst  $V_2O_5/TiO_2$ , *Chem. Eng. J.* 129 (2007) 167–172.