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Eco friendly dyeing of wool and cotton fabrics with reactive dyes (bifunctional) and its antibacterial activity

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ABSTRACT

The aim of this study is dyeing wool and cotton fabrics by synthesized reactive dyes (bifunctional) via chromophore system derived from pyrazolo [1,2-a] pyrazole 3-carboxylic acid fused systems in our previous work [1] as reactive dyes for cotton and wool fabrics via ecofriendly, Microwave technique, to enhance favorable properties especially color strength and light fastness with decrease of dyeing time. In addition, impart it antibacterial activity comparing with our previous conventional method dyeing properties and antibacterial activity were estimated. Wool and cotton fabrics were dyed by using the prepared reactive azo dyes under ordinary dyeing conditions by using microwave. The antibacterial activity of the prepared dyes were evaluated by using Inhibition zone method by using *S. aureus* as Gram-positive bacteria and *E. coli* as Gram-negative bacteria, taking tetracycline and ciprofloxacin as standard drugs. The prepared dyes showed more values of exhaustion and fixation, colour yields, fastness properties and antibacterial activity.

Keywords: bifunctional reactive dyes; Antibacterial activity; Pyrazole dyes; diazo dyes; Dyeing; wool; cotton

INTRODUCTION

In recent years, dyeing of some materials and modifications were conducted by using microwave radiation. The advantage of microwaves from convention methods, which it is use much less liquid, they can exhaust or save dyes and leave no waste of liquid dye. Microwave dyeing has other advantage such as less power consumption, easy production of desired shades; some synthetic dyes are being banned by the Western countries because its carcinogenic, toxic and polluting nature [2-10].

Progress in chemistry of reactive dyes were estimated to develop coupling of new heterocyclic components, which linked to the reactive systems through different binding linkages. The nature of such linkages depends on the structure of the heterocyclic chromophore and the substituents there in.

We have previously reported the synthesis of some novel azo disperse dyes used for dyeing of acetate and nylon fabrics with various bright colours and good fastness properties [11-13]. In addition we prepared new di azo reactive dyes for wool and cotton fabrics and evaluated its dyeing properties [14].

The aim of the present work is to dye wool and cotton fabrics by synthesized heterobifunctional monochlorotriazine/sulphato-ethylsulphone (MCT/SES) reactive dyes based on 1,5-dioxo pyrazolo[1,2-a]pyrazole3-carboxylic acid as chromophoric system in microwave and to estimate their antibacterial properties towards Gram positive and Gram negative bacteria to maximize their benefits.

MATERIALS AND METHODS

Chemicals

Hostapal CV (Clariant, Egypt) was used as a nonionic detergent. Albeal A (amphoteric leveling agent; Ciba) was used as an auxiliary for dyeing wool. 2,4-Diaminobenzenesulphonic acid (98%) and 1-aminobenzene-4- β -sulphatoethyl sulphone (PABSES) (96%) were obtained from Amar Impex, Mumbai, India. 4-Amino-2-diphenylamine-sulphonic acid (96%), 4-amino-azobenzene,3,4disulphonic acid (96%) were obtained from Isma Dyestuff and Chemical Co., Egypt. Cyanuric chloride (98%) and maleic acid (98%) were purchased from Merck Co., USA. All other chemicals used in this study were of laboratory reagent grade and applied without further purification.

Fabrics

Mill-scoured and bleached cotton fabric (130 g/m²; Misr El-Mahalla Co., Egypt), wool fabric (310 g/m²; Golden Tex Co., Egypt) were used throughout this work.

Synthesis of dyes

We are synthesized these dyes previously [1]

4-(2-(or3)-hydroxysulphonyl-aryloxy)5-oxo-1,2-dihydro-3-pyrazol carboxylic acid (dye intermediates a-c)

The dye intermediates **a-c** were synthesised by the reaction of 5-pyrazolo 3-carboxylic acid with 2,4-diaminobenzenesulphonic acid, 4-amino-2-diphenylamine-sulphonic acid and 4-amino-azobenzene,3,4disulphonic acid and 4-aminodiphenylamine-2-sulphonic acid diazonium chlorides, respectively. The pH was maintained at 6.5 by simultaneous addition of 2M sodium hydroxide solution and the coupling reaction completed within 2h at 0-5°C. The reaction mixture was acidified with diluted hydrochloric acid till precipitation, then the resulting dye intermediates **a-c** were filtered and dried under vacuum at 50°C. The chemical structures of the synthesised dyes **a-c** were confirmed by elemental analysis and spectral investigations. The following results were obtained:

4-(2-(or3)-hydroxysulphonyl-aryloxy)-7-amino-1,5-dioxypyrazolo[1,2-a]pyrazol-3-carboxylic acid (dye intermediates Ia-Ic)

The dye intermediates (**a**: 3.27 g; **b**: 4.03g; **c**: 4.96g; 0.01 mol) were dissolved in water (100 ml) at room temperature and the pH was adjusted to 7 using sodium carbonate solution. To these, ethylcyanoacetate (1.13 g; 0.01 mol) was added dropwise. The reaction mixtures were stirred under reflux for 2 h, maintaining the pH at 7-8, then the reaction was cooled to room temperature and the products were acidified with diluted hydrochloric acid till precipitation. The resulting intermediates **Ia-Ic** were filtered and dried in an oven at 40°C.

Synthesis of disazo heterobifunctional monochlorotriazine /sulphatoethylsulphone (MCT/SES) reactive dyes

7-Amino-1,5-dioxo 4-[2-(or3)-sodium sulphonato-4-aryloxy] -6-[5-[4-chloro-6-(β -sodiumsulphonatoethylsulphonyl-4-phenylamino)-1,3,5-triazine-2-ylamino]-2-sodiumsulphonato-1-phenylazo] pyrazolo[1,2-a] pyrazol-3-carboxylic acid 1-3 (Scheme 2).

The method was carried out by initial preparation of the MCT/SES diazonium salt: A suspension of cyanuric chloride (1.88 g; 0.01 mol) in acetone (20 ml) and crushed ice (10-20 g) was stirred at 0-5°C. A solution of 2,4-diaminobenzenesulphonic acid (1.91 g; 0.01 mol) in water (30 ml) at 5°C and pH 4.5-5 was slowly added to this suspension. The mixture was stirred for 2h at 0-5°C and pH 4.5. The reaction product was then treated with 1-aminobenzene-4- β -sulphatoethylsulphone PABSES (2.86 g; 0.01 mol) in water (50 ml) at pH 5.5-6, allowing the temperature to rise gradually to 30°C and the pH to 6.5-7. The reaction was completed within 4-5 h (stable pH). The solution was filtered, cooled to 0-5°C and then treated with 10 ml HCl/0.69 g NaNO₂ to produce the diazonium salt. The resulting solution of the diazonium salt was then added slowly to a stirred solution of the dye intermediates **Ia** (3.94 g; 0.01 mol), **Ib** (4.70 g; 0.01 mol) and **Ic** (5.63 g; 0.01 mol) at 0-5°C. The reaction mixture was stirred for further 2h at pH 5-6 and at 0-5°C. The desired reactive dyes **1-3** were precipitated by slow addition of sodium chloride (15% w/v), filtered and dried under vacuum at 40°C.

Dye 1: yellow, m.p. .300°C, yield 85 per cent, λ_{max} (H₂O) 417.5 nm

Dye 2: brick brown, m.p. .300°C, yield 78 per cent, λ_{max} (H₂O) 484.0

Dye 3: orange, m.p. . 300°C, yield 77 per cent, λ_{max} (H₂O) 487.0 nm:

Dyeing procedures

Here we successful to replace the dyeing convention method in our previous method [1] by ecofriendly microwave procedure; The microwave equipment used in this experiment was the Samsung M 245 with an output of 1,550 watts operating at 2450 MHz ; as follow

Dyeing of cotton

In dye bath containing 2 g of fabric at liquor ratio 40:1, 60 g/l Sodium sulphate and 20 g/l sodium carbonate for periods (1-5 minutes) in microwave

Dyeing of wool

The dyes were applied at different pH (3-7) , 5% ammonium sulphate and 1g/l albeal for periods (1-5 minutes) in microwave.

The dyeing was carried out in distilled water, then dyed samples were rinsed and extracted with 50 % DMF at boil for 15 minutes.

Measurements and testing**Dye exhaustion**

For all dyeings, the dye exhaustion was measured by sampling the dyebath before and after dyeing. The dye concentration (g/l) of the dyebath was measured on Shimadzu UV-2401PC UV/Vis spectrophotometer at λ_{\max} of the dye. The percentage of dye exhaustion (%E) was calculated using Eqn (1):

$$\%E = \left(\frac{C_1 - C_2}{C_1} \right) \times 100 \quad (1)$$

where C_1 and C_2 are the concentrations of the dyebath before and after dyeing.

Dye fixation

Measurement of the dye fixation was carried out by stripping the unfixed dye from the dyed material using 50 % aqueous dimethylformamide solution at the boil [15]. The stripping treatment was carried out repeatedly for 2 min periods using fresh aqueous DMF solutions until no further dye was removed. The percentage fixation (%F) of each dye was determined using Eq. (2).

$$\%F = \frac{C_1 - C_2 - C_3}{C_1 - C_2} \times 100 \quad (2)$$

where C_3 is the concentration of the extracted dye.

The total dye fixation (%T), which is the percentage of the dye chemically bound on the fabric relative to the total amount of dye used, was determined using Eqn (3).

$$\%T = (\%E \times \%F) / 100 \quad (3)$$

Colour strength

The relative colour strength (K/S) and CIELAB coordinates (L^* a^* b^*) of undyed and dyed cotton fabrics were determined using an Ultra Scan PRO spectrophotometer (Hunter Lab) with a D65 illuminant and 108 standard observer [16].

Fastness testing

The dyed samples were washed-off using 2 g/l nonionic detergent at 80°C for 30 min, and tested according to ISO standard methods (Methods of tests for colour fastness of textiles and leather, 5 th ed. Bradford: SDC, 1990). The specific tests were ISO 105-X12 (1987), ISO 105-C02 (1989), ISO 105-E04 (1989), and ISO 105-B02 (1988) corresponding to colour fastness to rubbing, washing, perspiration and light, respectively.

Evaluation of Antibacterial Activity in vitro:**Materials:**

Two bacterial strains from Bacterial Lab, Botany Department, the Faculty of women for Art, Science & Education, Ain Shams University, Cairo, Egypt were employed. They include *Staphylococcus aureus* (*S. aureus*) as Gram-positive (G +ve) bacteria and *Escherichia coli* (*E. coli*) as Gram-negative (G-ve) bacteria. *S. aureus* and *E. coli* were selected as test cells because they are the most frequent bacteria in the wound infection and represent Gram positive and Gram negative bacteria, respectively. Fresh inoculants for antibacterial assessment were prepared on nutrient broth at 37°C for 24 hours

Test Method:

The antibacterial activity of treated and dyed samples was determined against the test bacteria by disk diffusion method on an agar plate [17, 18]. Briefly, 1 cm diameter blended film samples were cut and put into 10 ml of nutrient agar, to which 10 μ l of microbe culture was inoculated, after the solidification. The plates were incubated at 37°C for 24 hrs, after which the diameter of inhibition zone were measured and recorded.

RESULTS AND DISCUSSION

Herein we compare the dyeing process of wool and cotton by reactive dyes **1-3** in microwave which give more values of fixation and exhaustion with short time compared with in conventional method [1]. Figure 1 indicate dye 1-3 fixation and exhaustion onto cotton at different time in microwave. The result indicate that the fixation and exhaustion increase in microwave technique than conventional method.

Figure 2 shows dyes fixation and exhaustion at different pH (3-7) for dyes 1-3. The results prove that the highest substantively of the dyes were found at low dyebath pH (pH 3) is attributed to the electrostatic interaction existed between dyes anionic sites and fiber NH_3^+ groups. At higher pH values (pH 4-5) leads to an increase in the number of sites available for covalent bonding via both of nucleophilic substitution and b-attack (MCT/SES dyes 1-3) mechanisms.

Otherwise, Figures 3,4 shows that there is a relation between K/S and dyeing time of wool and cotton in microwave respectively and it prove that the highest value of K/S for wool and cotton at 3 min. this result is refers to using microwave is saving time

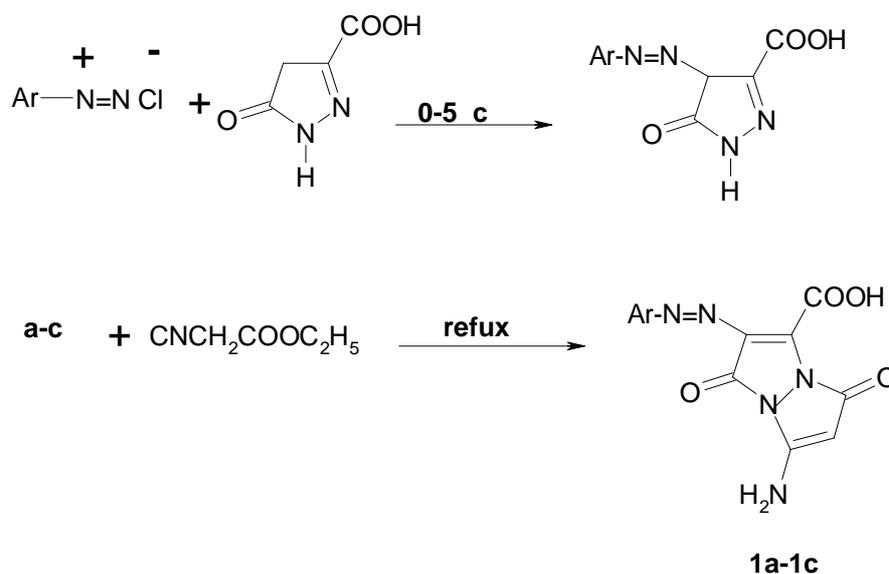
Colour strength and fastness properties

The colour fastness properties of the reactive dyes **1-3** on cotton, wool were estimated. Table II illustrate that the results of colour fastness, rubbing, washing and perspiration properties of these dyes ranged from excellent to good and are almost give similar values and depends on the fixed dye amount. In addition we obtain similar values of all dyes light fastness. This seems reasonable as all the dyes under investigation have approximately the same chromophoric system based on 1,5-dioxopyrazolo[1,2-a] pyrazole3-carboxylic acid

Table I Colour strength (K/S) and fastness properties of reactive dyes, SES 1-3 and MCT/SES 4-6, on different fabrics

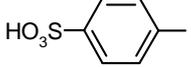
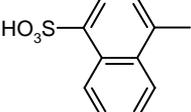
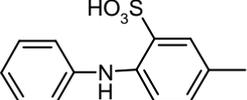
Dye No.	Fabric*	Fastness to rubbing		Washfastness**			Fastness to perspiration**						Light	
		Dry	Wet	Alt	SC	SW	Alkaline			Acidic				
							Alt	SC	SW	Alt	SC	SW		
1	C	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
	W	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
2	C	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
	W	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	5
3	C	4-5	4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	-4
	W	4-5	3-4	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4

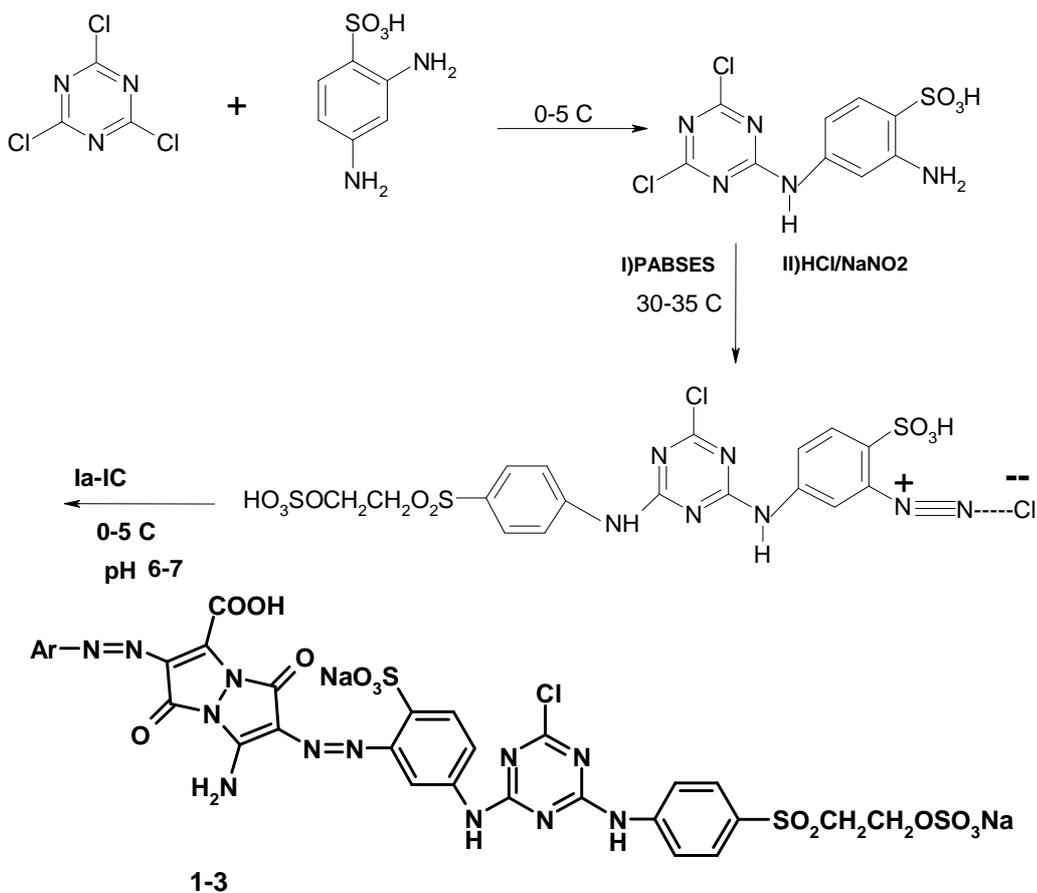
*C, Cotton; W, wool; S, silk; **Alt = alteration; SC = staining on cotton; SW = staining on wool



Scheme 1 Synthesis of dye intermediates a-c and Ia-Ic (for key see Table I)

Table I Identification of aryl radicals of the pyrazolone azo moieties for the dye intermediates (a-c and Ia-Ic) and reactive dyes (1-6)

Dye No.	Ar
a, Ia, 1,	
b, Ib, 2,	
c, Ic, 3,	



Scheme 2 Synthesis of disazo monofunctional SES reactive dyes 1-3 (System 1) and disazo heterobifunctional MCT/SES reactive dyes 4-6 (System 2) (for key see Table I)

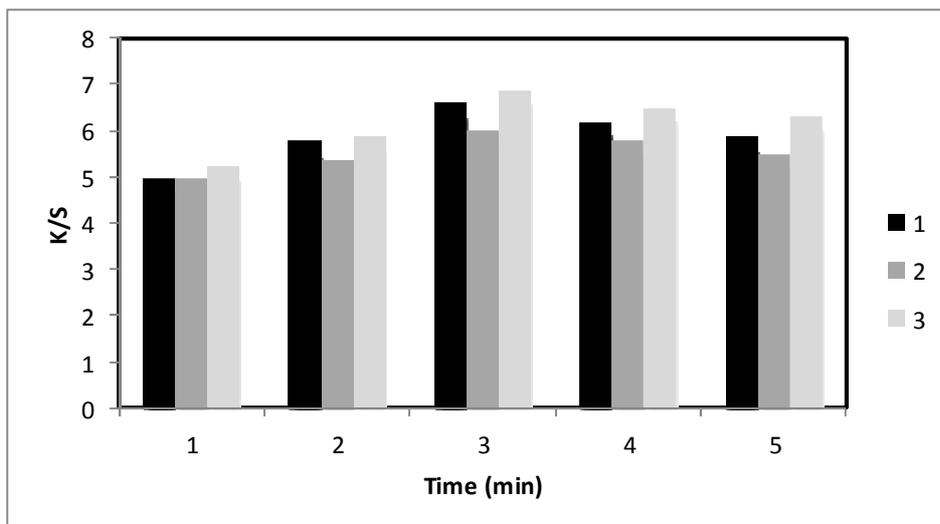


Figure 4 : Effect of dyeing time by microwave on cotton of reactive dyes 1-3

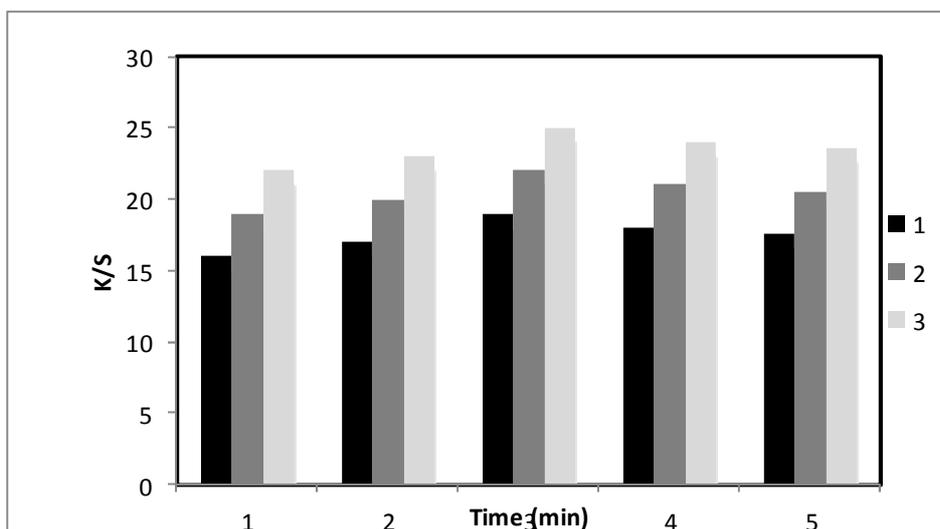


Figure 5: Effect of dyeing time by microwave on wool of reactive dyes 1-3

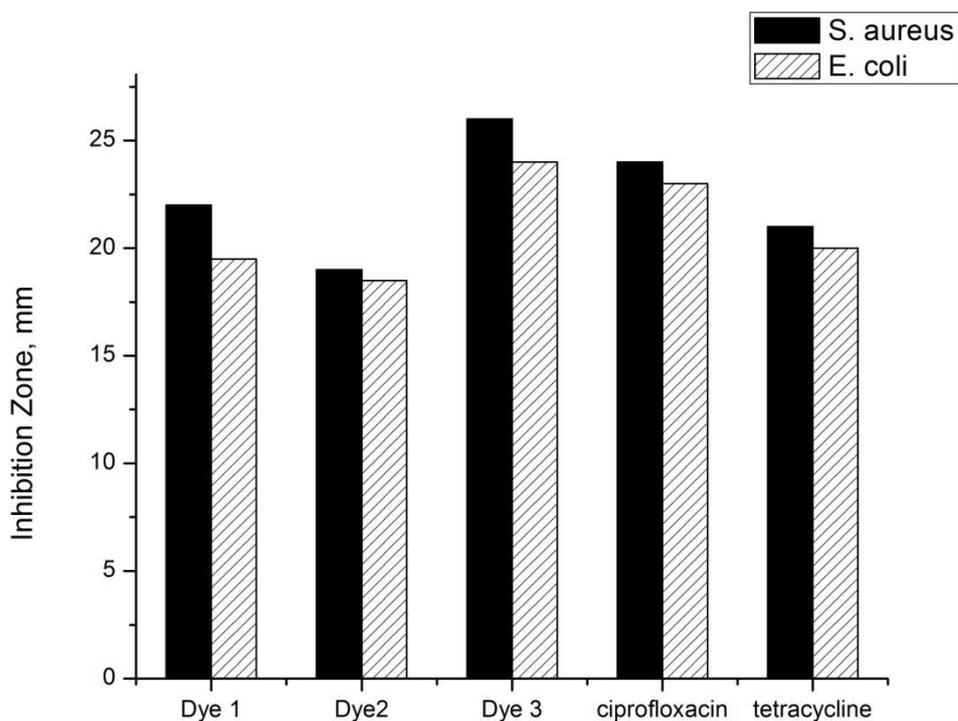
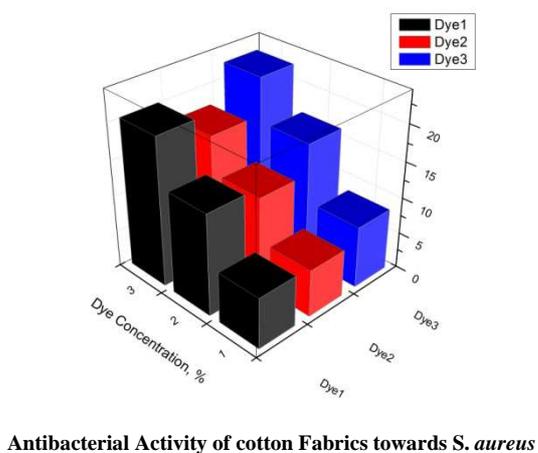
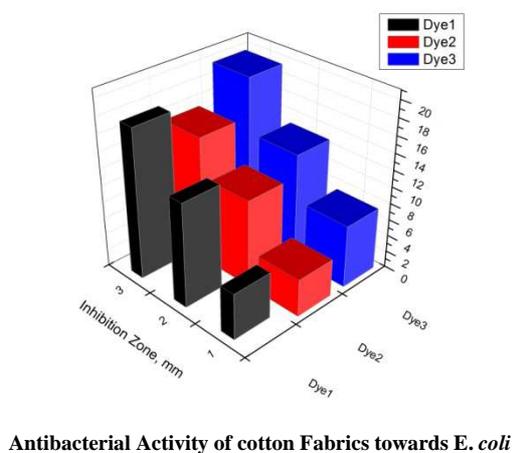


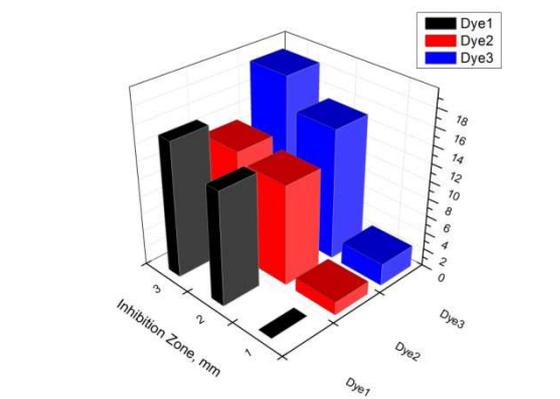
Figure 6: Results of antibacterial test for reactive dyes solution



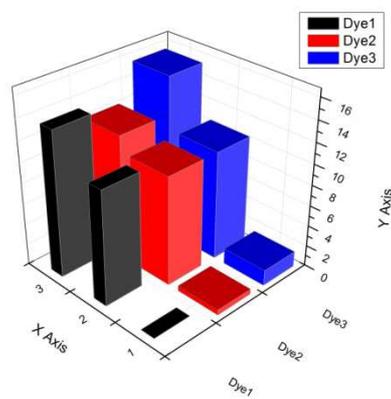
Antibacterial Activity of cotton Fabrics towards *S. aureus*



Antibacterial Activity of cotton Fabrics towards *E. coli*



Antibacterial Activity of Wool Fabrics towards *S. aureus*



Antibacterial Activity of Wool Fabrics towards *E. coli*

Figure 7: Results of antibacterial test for cotton and wool fabric dyed with reactive dyes 1,2 and 3 against *Staphylococcus aureus* and *Escherichia coli*

Antibacterial activity of reactive dyes *in vitro*:

The antibacterial activity of the prepared reactive dyes were estimated *in vitro* through Inhibition method by using two bacterial strains, *S. aureus* as Gram-positive bacteria and *E. coli* as Gram-negative bacteria, taking tetracycline and ciprofloxacin as standard drugs.

Figure 6 shows that dye **1** and **3** showed an excellent activity towards *S. aureus* and slight less activity towards *E. coli* although dye **2** were slight less activity towards both *S. aureus* and *E. coli* with respect to standard drugs. It is apparent that these dyes are bactericidal not bacteriostatic

Dyes concentration effects on antibacterial properties were studied (Figure7). Zone of inhibition was recorded in each case. The results of undyed samples show that they does not inhibit bacterial activity, although dyed fabrics inhibit bacterial growth as is evident from the lack of growth under all treated samples. It was observed that antibacterial properties of the prepared dyes expressed in inhibition zone increases as the concentration of dyes increased The order of antibacterial properties were: **dyes 1 = dye3 > dye 2**.

These dyes contains -NHN= and -CONH- groups in their molecular structure which have positive charges that allow dye molecules to be adsorbed readily onto bacterial surfaces, and then penetrate the cell membrane, followed by destruction of cell membranes and leakage of cell inclusion body causing bacteria death. These dyes showed better efficacy against the *S. aureus* than *E. coli* due to their cell wall structure. [19-21]. The antibacterial activity of dyes **1** and **3** are more than that of dye **2** due to presence of phenyl and 4-bromophenyl groups in its molecule which increase conjugation and carbon skeleton [22]. In addition, it was clear that from table 4 that antibacterial properties of all cotton-dyed samples shows higher than that for cotton-dyed samples due to fabric nature and structure.

CONCLUSION

- We successfully prepare reactive dyes (bifunctional) previously and dyed wool and cotton fabrics in conventional method
- But now, we are using microwave techniques in dyeing to decrease dyeing time and this technique is safely to environment.
- The results of dyeing in microwave show higher exhaustion and fixation values, colour yield and fastness properties than in conventional methods.
- In addition, we use the dyed cotton and wool fabric as antimicrobial activity toward Gram-negative and Gram-positive

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