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Utilizing Semi-Natural Antibacterial Cellulose to Prepare Safe Azo Disperse Dyes and Their Application in Textile Printing

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Abstract: The present study describes the synthesis of three new antibacterial azo disperse dyes from different diazotized aryl amines (aniline, 2-aminothiazole, and sulfathiazole), followed by their reactions with a novel nontoxic antibacterial cyanoacetyl microcrystalline cellulose derivative (**a**) as a coupling component. The structures of the dyes were confirmed and elucidated by FTIR and ^{1}H-NMR spectroscopy. The new dyes were also tested for antibacterial activity and toxicity, and they were utilized for silk screen printing polyester and nylon 6 fabrics. The color strength and fastness properties of the dyes have been investigated, and they exhibited high resistance to washing, perspiration, and rubbing as well as fastness to sublimation and light. Moreover, the new dyes were tested for antibacterial activity on the printed polyester and nylon 6 fabrics.

Keywords: Azo dyes, Antibacterial microcrystalline cellulose, Fastness properties, Polyester dyeing

Introduction

Azo dyes represent the most important class of synthetic dyes [1,2] because they can be synthesized easily and have various industrial applications in different fields, such as dyeing textile fibers, cosmetics, biological studies, and paper printing [3,4]. Azo disperse heterocyclic dyes are common for dyeing and silk screen printing polyester and nylon 6 fibers because they show suitable color brilliance, higher chromophoric and tinctorial strength, a desirable color range, and good sublimation fastness properties [5].

In recent decades, continuous attempts to replace synthetic dyes prepared from petrochemicals with eco-friendly natural dyes have been fruitful [6-8]. Currently, using nontoxic, antimicrobial, and eco-friendly azo dyes on textiles is preferred because they are not expected to cause environmental problems [9,10]. In this context, cellulose, a polymer of glucose, is a renewable and biodegradable natural polysaccharide polymer. It is also a versatile starting material for different chemical transformations, and a large number of different cellulose derivatives have been used in industries, such as the food, cosmetic, printing, oil well drilling, textile, and pharmaceutical industries [11]. Cellulose fibers give a medium for microorganisms to grow because of their large surface area and ability to retain moisture, which represents a disadvantage in some applications. Therefore, several chemical treatments have been explored to increase the antimicrobial activity of cellulosic materials [12-14].

Recently, some azo cellulose derivatives were successfully synthesized [15,16]. Based on previous reports describing the versatility of active methylene groups as nucleophiles in reactions with aldehydes, nitrous acid, and diazonium salts [17-19], the current study was undertaken with the primary objective of prepare nontoxic antibacterial azo compounds via diazotization of a novel nontoxic antibacterial cyanoacetyl microcrystalline cellulose derivative [20,21] utilizing different aryl amines, especially sulpha derivatives with known antibacterial properties [22-24].

In addition, we inspected whether azo groups located on the spacer of cellulose would stimulate and exhibit high affinity for silk screen-printed polyester and nylon 6 fabrics with acceptable and good fastness properties, as this could afford colored sterile and/or biologically active fabrics that could be used in various fields [25].

Experimental

Materials

Chemicals

The following chemicals have been used: aniline, 2-aminothiazole, sulfathiazole, sodium dihydrogen phosphate, sodium chloride, sodium nitrite, and sodium acetate trihydrate. They were analytical-grade products purchased from Sigma-Aldrich, Merck, and BDH. The other chemicals and solvents used in this study were of laboratory reagent grade.

Fabrics

Polyester and nylon (150 g/m^2) were supplied by Egyptian and developing Co., Cairo, Egypt.

Thickening Agents

DaicoThic 1600, a synthetic thickener for azo disperse silk screen printing, was kindly supplied by Daico company.

Characterization

The progress of all reactions was monitored using thin-layer chromatography (TLC) with 0.2-mm thick TLC plates

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(aluminum-backed, silica gel 60 F245) obtained from Merck, and the spots were located by UV light. The melting points of the synthesized compounds were determined by the open capillary method and are uncorrected. FT-IR spectra were obtained with a JASCO FTIR-4100 E Fourier transform infrared spectrometer (Japan) operated in absorption mode in the wave number range of 4,000-400 cm^{-1} by mixing with KBr (potassium bromide) to form discs. ^{1}H-NMR spectra were determined using a Jeol JMS-AX 500 MHz instrument with DMSO-d_6 as the solvent and TMS as the internal standard. Chemical shifts are reported in δ (ppm). Thermo Finnigan MAT95XP and Thermo Scientific LTQ Orbitrap XL mass spectrometers were used, and the UV-Vis spectra were recorded on a UV-2401PC spectrometer.

General Procedure for the Synthesis of 2-(2-Aryl-Hydrazono)Cyanoacetyl Microcrystalline Cellulose Derivatives (b-d) [21]

To a stirred suspension of 0.01 mole of (aniline, 2-aminothiazole, or sulfathiazole) in hydrochloric acid (1.1 m*l*) was added a solution of sodium nitrite (0.6 g) over a period of 15 min. The temperature was maintained at 0-5 °C with stirring, and after completion of the addition, the mixture as stirred for an additional 5 min. The diazonium salt solution was poured into a cooled mixture of compound (**a**) (2 g) and sodium acetate trihydrate (3.5 g) in DMSO (20 m*l*). The resulting mixture was stirred for 1 h and then poured into cold water. The obtained precipitate was filtered off, washed with water and dried.

2-(2-Phenylhydrazono)Cyano Acetyl Microcrystalline Cellulose (b)

Orange solid; yield (77 %), m.p. (charring at 170-180 °C); IR (KBr, cm^{-1}) ν: 3446 (OH), 3230 (NH), 3052 (phenyl), 3045 & 2920 (CH & CH_2), 1600 (C=N), 1736 (CO), 2200 (C≡N); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.9-2.0 ppm (s, 3H, acetyl protons), 3.5-5.1 ppm (m, 7H, cellulose protons), 7.2-7.9 ppm (m, 4H, aromatic protons), 12.5 ppm (br s, 1H, HN D_2O exchangeable proton); MS: m/z (%): 92 (100 %), 162 (15 %) and 144 (84 %).

2-(2-Thiazol-2-Yl)Hydrazono)Cyano Acetyl Microcrystalline Cellulose (c)

Black solid; yield (72 %), m.p. (>300 °C); IR (KBr, cm^{-1}) ν: 3318 (OH), 3190 (NH), 2925 (CH), 1600 (C=N), 1746 (CO), 2200 (C≡N); ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.9-2.0 ppm (s, 3H, acetyl protons), 3.5-5.1 ppm (m, 7H, cellulose protons), 6.5 ppm (d, 1H, J=4.7 Hz, thiazole H_4), 6.8 ppm (d, 1H, J= 4.7 Hz, thiazole H_5), 12.2 (br s, 1H, NH D_2O exchangeable proton).

2-(2-(4-(N-Thiazol-2-Ylsulfamoyl)Phenyl)Hydrazono) Cyanoacetyl Microcrystalline Cellulose (d)

Deep-red solid; yield (74 %), m.p. (charring 240-250 °C); IR (KBr, cm^{-1}) ν: 3441 (OH), 3230 (NH), 3050 (phenyl), 2911 (CH), 1600 (C=N), 2220 (C≡N), 1728 (CO), 1600 (C=C). ^{1}H-NMR (500 MHz, DMSO-d_6) δ: 1.9-2.1 ppm (s, 3H, acetyl protons), 3.5-5.1 ppm (m, 7H, cellulose protons), 6.5 ppm (d, 1H, J=4.7 Hz, thiazole H_4), 6.8 ppm (d, 1H, J=4.7 Hz, thiazole H_5), 7.2-7.9 ppm (m, 4H, aromatic protons), 12.5 ppm (br s, 1H, NH HN D_2O exchangeable proton). MS:m/z (%): 92 (100 %), 162 (15 %), 334 (84 %).

Textile Printing

Preparation of Printing Paste

The printing paste was prepared using the proportions shown in Table 1.

Printing Technique

The conventional silk screen printing technique was used.

Fixation

The printed fabrics were thermally fixed at 180 °C for 5 min using an automatic oven (Wener Mathics Co., Switzerland).

Reduction Clearing and Washing

The washing of the printed fabrics was carried out as follows: The fabric was rinsed in cold water, and soaped at 60 °C with 2 g/*l* Hostapal CV (nonionic detergent) for 20 min. Reduction clearing with 2 g/*l* hydrosulfite, 2 g/*l* sodium hydroxide (32.5 %), and 2 g/*l* Hostapal CV (nonionic detergent) at 40-70°C, then rinsing at 60-70 °C was followed by cold rinsing.

Fastness Testing

The printed samples were subjected to rubbing, washing, perspiration, and light according to the standard ISO methods, namely, ISO 105-X12 (1987), ISO 105-co4 (1989), ISO105-EO4 (1989), ISO 105-BO2 (1988), respectively.

Acute Dermal Toxicity

Animals and Treatment

Male albino Wistar rats (*Rattusnorvegicus*) weighing 150-155 g were obtained from the Animal Breeding House (ABH) of the National Research Center (NRC), Dokki, Cairo, Egypt. The animals were housed in clean plastic cages in the laboratory animal room (22±1 °C) and provided the standard pellet diet and tap water *ad-libitum*. They were housed with a minimum relative humidity of 45 % and a 12 h dark/light cycle. The rats were allowed to acclimate to the laboratory conditions for 7 days prior to dosing. The newly prepared dyes were dissolved in DMSO and used for

Table 1. The components of the printing paste

Dye	40 g
Thickener	2-5 g
Lyprint	3 g
Sodium dihydrogen phosphate	5 g
Sodium chloride	10 g
Water	x
Total	1000 g

dermal studies with a fixed volume of 0.5 m*l*/rat. The animals were randomly divided into four groups with five rats in each group. One group was used as the control. The other groups were treated with the newly prepared dyes (**b**, **c**, and **d**) at a dose of 500 mg/kg b. wt. The mortality of the treated rats was recorded after 24 h. The fur was removed from the dorsal/flank area of the test animals (10 % of the total body surface area). The tested dyes were held in contact with the skin with a porous gauze dressing for 24 h. After dosing, the rats were observed for the first 30 min, then at 2, 4, 6, and 24 h, and then daily for 7 days. The experimental protocols and procedures were performed with approval from the ABH and the Local Ethics Committee at the National Research Centre (NRC), Dokki, Cairo, Egypt, and protocols conformed with the Guide for the Care and Use of Laboratory Animals (NRC, 1999) [26,27].

Results and Discussion

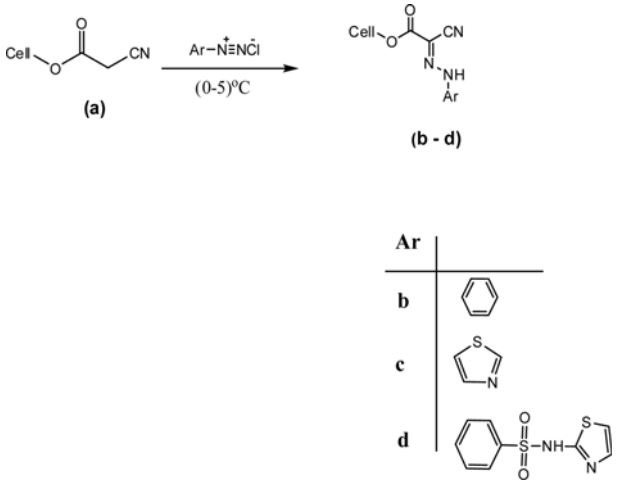
The present study describes the design, synthesis and textile printing evaluation of newly developed, safe antibacterial azo disperse dyes, and the addition of a novel cyanoacetyl microcrystalline cellulose derivative [20] to diazonium salts of aromatic amines in the presence of sodium acetate was used to avoid the formation of the corresponding oximino derivatives as side products [28,29]. The obtained cellulosic dyes with branched chromophoric azo dye moieties are illustrated in Scheme 1.

Spectral Characteristics

The FT-IR spectra of the azo compounds (**b**, **c**, and **d**) showed bands from 3230-3050 cm^{-1} attributable to -NH and -OH groups [30,31] and bands at 3049 cm^{-1} for aromatic CH moieties. The bands at 2729-2920 cm^{-1} were attributed to alkyl groups. The cyano group resulted in a band at ~2200 cm^{-1}, while the carbonyl absorption as a sharp band appeared at ~1736 cm^{-1}. The band of the azo C=N appeared at ~1600 cm^{-1}, while those of the SO_2 group in compound **d** appeared at 1155-1136 cm^{-1} and 1083-1053 cm^{-1}.

The ^{1}H-NMR spectra of azo compounds **b**, **c**, and **d** revealed signals at 1.9 and 2.0 ppm attributable to cellulose acetyl protons, signals at 3.5-5.1 ppm for the cellulose protons [32], and signals at 12.5 ppm for the D_2O-exchangeable NH. In addition, the signals appearing at 6.5 and 6.8 ppm in the spectra of compounds **c** and **d** were attributed to thiazole protons [33], and these signals along with the aromatic protons at 7.2-7.9 ppm in the spectra of compounds **b** and **d** confirmed their structures. It is worth mentioning that the signal of the parent cyano-active methylene group disappeared in the spectra of the azo derivatives, as expected [34].

The mass fragmentation patterns of products **b** and **d** showed ion fragments at m/z 162 attributable to the fragmentation of glucose the residue in the cellulosic chain and at m/z 92, which represents the aniline moiety in product **b**. These signals along with the ion fragment at m/z 144, indicating a formula of $[C_8H_6N_3]^+$, are consistent with the anilino cyano hydrazone moiety of **b**. The ion fragment of m/z 334 is consistent with the weight of $[C_{12}H_9N_5O_3]^+$, a



Scheme 1. Synthetic route to dyes **b**-**d**.

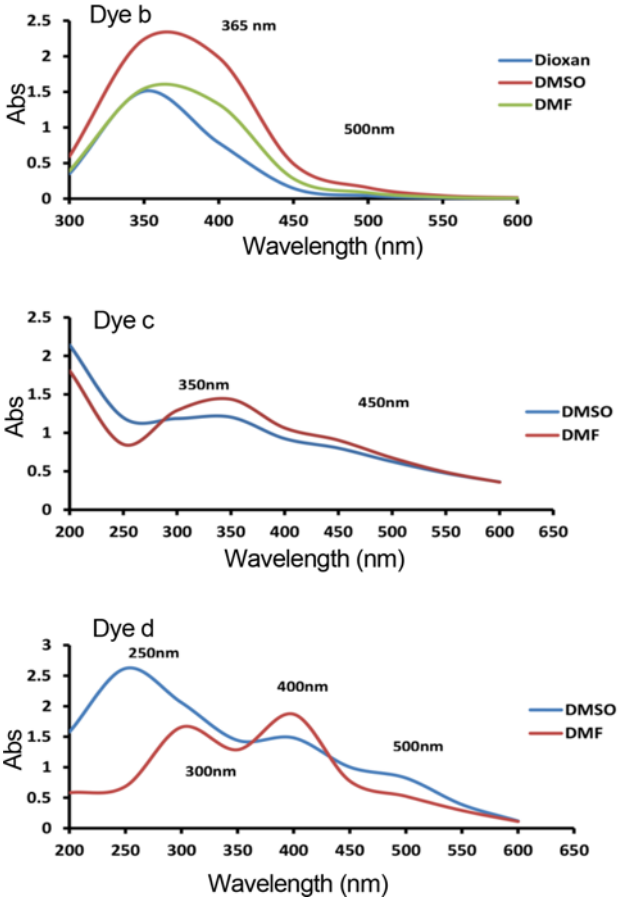


Figure 1. UV/Vis absorption spectra of prepared dyes **b**, **c**, and **d**.

fragment of **d** attributed to an N-thiazol-2-ylsulfamoyl) phenyl) hydrazono) cyanoacetyl fragment.

UV-Vis Spectra

The UV-Vis absorption spectra of dyes **b**, **c**, and **d** (c=1.9 $\times 10^{-6}$ M) in three solvents (dioxane, DMSO, and DMF) are shown in Figure 1. The UV-Vis absorption spectrum of dye **d** in polar solvent (DMF or DMSO) revealed that it absorbs radiation in both the visible range (ca. 400 and 500 nm) and in the UV range (300 nm) in DMF but with a blue shift to 250 nm in DMSO due to its high polarity. Similarly, dye **c** absorbs in the UV range at 350 nm and in the visible range at ca. 450 nm in both solvents. The absorption of **d** shows a bathochromic shift relative to that of **c** (ca. 500 nm) because its sulfathiazole moiety has more conjugated double bonds than its corresponding thiazole residue in dye **c**.

An attempt to dissolve dyes **c** and **d** in a less polar solvent (dioxane) was unsuccessful.

In the case of dye **b** (Figure 1) it was soluble in dioxane, and its spectrum showed absorptions in both the UV and visible ranges at ca. 365 nm and 500 nm, respectively. In polar solvent (DMF or DMSO), it mainly absorbs in the UV range. In this context, it has been reported that microcrystalline cellulose (the parent backbone in the presented dyes) absorbs radiation in both the UV and visible ranges [35].

Acute Dermal Toxicity

The results showed no mortality or signs of toxicity in rats treated with the tested dyes. In addition, no changes in the skin, fur, eyes, or behavior of the test animals were recorded.

Color Strength (*K/S*)

The color strength data of the printed samples are shown in Tables 2 and 3 and were recorded by a light reflectance technique using a Perkin-Elmer UV/Vis spectrophotometer (Model, Lambda 3B). The color strength (*K/S* value) was assessed using the Kubelka-Munk equation.

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

where R=decimal fraction of the reflection of the dyed fabric, K=absorption coefficient, and S=scattering coefficient.

Fastness Properties [36-38]

The color parameters of the silk screen-printed polyester and nylon 6 fabric samples were investigated and are recorded in Tables 4 and 5. The data in the tables show that the color strength of the printed polyester fabric (expressed

Table 2. Color assessment of the polyester samples printed with the prepared dyes

Dye	Absorption [λ_{max} (nm)]	*K/S*	L^*	a^*	b^*
b	355	8.83	65.57	7.72	30.96
c	380	10.14	22.76	16.23	14.24
d	365	2.85	88.63	1.70	5.89

Table 3. Color assessment of the nylon samples printed with the prepared dyes

Dye	Absorption [λ_{max} (nm)]	*K/S*	L^*	a^*	b^*
b	365	6.63	74.55	6.26	17.90
c	380	10.71	84.30	11.53	45.35
d	355	8.53	90.61	2.09	2.82

Table 4. Fastness properties of the polyester fabric printed with dyes **b-d**

Sample	Light fastness	Washing fastness[a)]		Rubbing		Perspiration fastness[a)]			
						Acidic		Alkaline	
		St.	Alt	Wet	Dry	St.	Alt	St.	Alt.
b	6	3-4	4	3-4	4	4	4	4-5	4
c	7	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
d	7	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5

[a)]Alt.=alteration in color and St.=staining on cotton.

Table 5. Fastness properties of the nylon 6 fabric printed with dyes **b-d**

Sample	Light fastness	Washing fastness[a)]		Rubbing		Perspiration fastness[a)]			
						Acidic		Alkaline	
		St.	Alt	Wet	Dry	St.	Alt	St.	Alt.
b	6	3-4	4	3-4	4	4	4	4-5	4
c	6	4-5	4-5	4-5	4-5	4-5	4-5	4-5	4-5
d	5	4-5	4-5	4	4-5	4-5	4-5	4-5	4-5

[a)]Alt.=alteration in color and St.=staining on cotton.

as *K/S*) depends on the nature of the substituents attached to the aryl azo colorant moiety of the prepared dye. Dyes **b-d** possess high color strengths, and they revealed good results. The polyester and nylon 6 fabric samples silkscreen-printed using prepared dyes **b-d** were thermally fixed at 180 °C for 5 min. The fixation temperature plays an important role in facilitating the mobility of the dye molecules and increases the rate of their transfer from the printed film into the fabric.

Washing Fastness

The washing fastness properties, based on the rate of movement of the prepared dyes out of polyester and nylon 6 fabrics during washing, depend on many factors, such as solubility of the dye in water, the molecular size of the dye, the nature of mechanical link between the dye and the fibers, and the nature of the charge and its location on the dye molecules and fabrics, which are affected by the presence of electron-donating or electron-withdrawing substituents. The washing fastness properties for the printed polyester fabrics, including alterations and stain on cotton, are good for the printed polyester and nylon 6 fabrics.

Perspiration Fastness

The magnitudes of the removal of the presented dyes from polyester and nylon fabrics under the influence of perspiration (alkali and acidic solutions) are recorded in Tables 4 and 5. The results indicate that dye removal is mostly dependent on the molecular weight of the dye and the binding force between the dye and the fabric. Generally, all the printed samples showed good to very good perspiration fastness values.

Rubbing Fastness

The recorded numerical data are an indication of the removal of loosely adhered dye molecules from the surface of the polyester and nylon 6 fabrics. The obtained values indicate higher rubbing fastness for high-molecular-weight dyes. Thus, these dyes gave very good rubbing fastness results.

Light Fastness

The synthesized dyes demonstrated light fastness values varying from good to very good, depending on the molecular structure of the dye and its aggregation within the polyester and nylon fibers. It also increases with the strength of the color of the dye. According to the AATCC test method, dyes **b-d** showed better light fastness on polyester than on nylon 6 fabrics.

Fastness to Sublimation

The sublimation fastness test [38] was conducted using an iron tester (Yasuda No. 138), and the results are shown in Tables 6 and 7. Sublimation fastness is a very important requirement for dyed or printed polyester and nylon fabrics. The samples were placed between two pieces of undyed cotton and polyester fabrics, all of equal diameters, and then treated at 180 °C and 210 °C for 1 min. The migration or removal of the azo disperse dyes from the surface of the polyester and nylon fabrics completely depended on the heat treatment. The changes in the undyed polyester-cotton and nylon-cotton fabrics used for the sublimation fastness tests generally showed good results according to the international geometric grayscale.

Antimicrobial Activity

The biological activity of the cyano acetyl microcrystalline cellulose, its dyes and the dyed fabrics were evaluated against Gram-positive (G+) (*Bacillus subtilis*and *Staphylococcus aureus*) and Gram-negative (G-) (*Escherichia coli* and *Pseudomonas aeruginosa*) bacterial pathogens.

The antimicrobial activities of the tested samples were determined using a modified Kirby-Bauer disc diffusion method [39]. Plates inoculated with Gram (+) bacteria and Gram (-) bacteria were incubated at 35-37 °C for 24-48 hours. The antimicrobial activities were evaluated by measuring the zone of inhibition against the test organisms and comparing with that of a standard [39].

The results in Table 6 show that cyanoacetyl microcrystalline cellulose has moderate antibacterial activity, while its novel dyes showed synergistic antibacterial activities. Table 7 shows that after washing four times, the polyester fabrics

Table 6. Sublimation fastness properties of the polyester fabric printed with dyes **b-d**

Sample	Sublimation fastness at 180 °C	Sublimation fastness at 210 °C	Staining on fabric after sublimation polyester	Staining on fabric after sublimation cotton
b	4-5	4	4	4
c	4	3-4	3-4	3-4
d	4	4	4-5	4-5

Table 7. Sublimation fastness properties of the nylon fabric printed with dyes **b-d**

Sample	Sublimation fastness at 180 °C	Sublimation fastness at 210 °C	Staining on fabric after sublimation nylon	Staining on fabric after sublimation cotton
b	4-5	4	4	4
c	4	3-4	3-4	3-4
d	4	4	4-5	4-5

Table 8. Inhibition zone (mean diameter of the disc in mm) as a criterion of the antibacterial activities of cyanoacetyl microcrystalline cellulose and the new disperse dyes

Sample	Bacterial species			
	Inhibition zone diameter (mm/mg sample)			
	G^+		G^-	
	Bacillus subtilis	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas aeruginosa*
Ampicillin (Standard antibacterial agent)	26	21	25	26
a	10	10	0.0	10
b	16	13	13	11
c	11	12	11	11
d	12	13	14	13

Table 9. Inhibition zone (mean diameter of the disc in mm) as a criterion of the antibacterial activities of the fabrics dyed with the new disperse dyes after 4 washes

Sample	Inhibition zone diameter (mm/mg sample)			
	G^+		G^-	
	Bacillus subtilis	*Staphylococcus aureus*	*Escherichia coli*	*Pseudomonas aeruginosa*
Polyester fabric printed dyed with (**b**)	12	13	12	10
Polyester fabric printed dyed with (**c**)	11	12	10	11
Polyester fabric dyed with (**d**)	12	13	11	13
Nylon 6 fabric printed dyed with (**d**)	11	11	12	12

dyed with the prepared dyes, especially dye **d**, have enhanced antimicrobial activities against the test pathogens.

Conclusion

Azo dyes were synthesized utilizing novel seminatural nontoxic antibacterial cyanoacetyl microcrystalline cellulose. Polyester and nylon 6 fabrics were silk screen printed with the new dyes. The color measurement and fastness properties of the prepared dyes showed they were highly resistant to washing, perspiration, and rubbing and that they had good light fastness. The performance, toxicity, and antibacterial properties of the newly synthesized cellulosic azo dyes indicate they are safe disperse dyes with improved applicability and antibacterial properties on textiles. Further investigations utilizing π-systems containing amines are in progress.

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