(REFEREED RESEARCH)

AN INVESTIGATION OF FASTNESS AND ANTIBACTERIAL PROPERTIES OF COTTON FABRIC COLOURED WITH WATER-SOLUBLE ZINC PHTHALOCYANINE CONTAINING AZO GROUPS

AZO GRUPLARI İÇEREN SUDA ÇÖZÜNÜR ÇİNKO FTALOSİYANİN İLE BOYANAN PAMUKLU KUMAŞIN HASLIK VE ANTİBAKTERİYEL ÖZELLİKLERİNİN İNCELENMESİ

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ABSTRACT

Main purpose of this research is to investigate dyeing properties, colour fastness values (light, water, perspiration, chlorinated water, rubbing, washing) and antibacterial activity of cotton fiber fabric dyed with water-soluble zinc phthalocyanine containing azo groups (Azo-ZnPc). It is expected that zinc metal ion and azo groups present simultaneously in one phthalocyanine (Pc) structure can ensure antibacterial effect on cotton fabric. Literature survey shows that this Azo-ZnPc structure was not used before as a dyestuff in textile colouration. Therefore, synthesis and investigation some properties of this dye could be worthwhile. In this study firstly, the Azo-ZnPc was synthesized and the structure was verified with FT-IR, UV/vis, mass spectra and ^{1}H-NMR, ^{13}C-NMR studies. Afterwards, the cotton fabric modified with a cationic auxiliary was dyed with the Azo-ZnPc in the presence of sodium carbonate via exhaustion process. Finally, the colour fastness values were determined according to ISO standards and color strength (K/S values), L, a*, b*, C*, h* values measurements were performed. Antibacterial properties of the uniformly green coloured fabric were examined according to AATCC 100 standard. Significant reduction of Staphylococcus aureus (S. aureus) and Klebsiella pneumoniae (K. pneumoniae) bacteria, rated as 99.99 %, 99.74 %, respectively, were observed on cotton fiber fabric.

Keywords: Antibacterial, cotton, phthalocyanine, azo group, zinc.

ÖZET

Araştırmanın temel amacı, azo grupları içeren suda çözünebilen çinko ftalosiyanin (Azo-ZnPc) ile boyanmış pamuklu kumaşın boyanma özelliklerini, renk haslık değerlerini (ışık, su, ter, klorlanmış su, sürtme, yıkama) ve antibakteriyel aktivitesini incelemektir. Bir ftalosiyanin (Pc) yapısında aynı anda bulunan çinko metal iyonu ve azo gruplarının pamuklu kumaş üzerinde antibakteriyel etki sağlayabileceği düşünülmüştür. Literatür araştırması, bu Azo-ZnPc yapısının tekstil renklendirilmesinde bir boyarmadde olarak önceden kullanılmadığını göstermektedir. Bu sebeple, bu boyanın sentezi ve bazı özelliklerinin incelenmesi değerli olabilir. Bu çalışmada ilk olarak, Azo-ZnPc sentezi gerçekleştirilmiş ve yapısı; FT-IR, UV/vis, kütle spektrumları ve ^{1}H-NMR, ^{13}C-NMR çalışmaları ile doğrulanmıştır. Daha sonra, bir katyonik yardımcı madde ile modifiye edilmiş pamuklu kumaş, çektirme prosesiyle sodyum karbonat varlığında Azo-ZnPc ile boyanmıştır. Son olarak, renk haslık değerleri ISO standartlarına göre belirlenmiş ve renk verimi (K/S değerleri), L, a*, b*, C*, h* değerlerinin ölçümleri elde edilmiştir. Homojen biçimde yeşil renge boyanan kumaşın antibakteriyel özellikleri AATCC 100 standartlarına göre incelenmiştir. Staphylococcus aureus (S. aureus) ve Klebsiella pneumoniae (K. pneumoniae) bakterilerinde, sırasıyla %99.99, %99.74 gibi, önemli derecede azalma gözlenmiştir.

Anahtar Kelimeler: Antibakteriyel, pamuk, ftalosiyanin, azo grubu, çinko

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1. INTRODUCTION

Phthalocyanines have a two-dimensional 18-π electron conjugated system, in which more than 70 different metal and also non-metal ions can be incorporated. A number of modications can be made in the macrocycle either by introduction of different central ions or by substitution of functional groups at the peripheral sites of the ring [1, 2].

Unsubstituted phthalocyanines are not very soluble and tend to aggregate in solution; however, the addition of peripheral chains can increase solubility, processibility, and facilitate the formation of discotic mesophase [3].

They exhibit unique properties such as excellent semiconductivity, photoconductivity, chemical stability and optical absorption in the UV-Vis region [4]. This versatility gives rise to many different application types such as catalysts, liquid crystals, electrochromic and photochromic substances, datastorage systems, photodynamic cancer therapy agents, photoactive units, solar cells, chemical sensors and nonlinear optical devices [5].

Phthalocyanines are widely used as blue and green colourants in a wide range of paint, printing ink and plastic applications for decades [6, 7]. $Cu^{II}Pc$ and its derivatives are important colourants since they exhibit good chemical (Cu^{II} fits well in the ligand) and photochemical (Cu^{II}, in contrast to Zn^{II}, has an open d electron configuration and therefore bad photo-excited states.) properties in the monomolecular dissolved or aggregated state [7]. The unsubstituted CuPc comprises around 21% of the world market for pigments, and it is the most important blue pigment used [8].

In the last few decades, many antimicrobial textile products have been developed with the usage of different synthetic antimicrobial agents such as triclosan, metal and their salts, organometallics, phenols and quaternary ammonium compounds due to the increased awareness for healty lifestyle and only few of these products are commercially available [9].

Antibacterial properties of metal ions such as copper (Cu^{+2}), ferric(Fe^{+2}), zinc (Zn^{+2}), silver (Ag^{+}) have been investigated and demostrated in previous studies [10-13]. Rajendran *et al.* [14] stated that cotton fabric finished with zinc oxide nanoparticles had significant antibacterial activity against *S. aureus* in both qualitative and quantitative tests.

Several reports show the antimicrobial effect of metallophthalocyanines against several species of bacteria in literature [15-21]. Phthalocyanines are effective photosensitive substances. Following their irradiation larger quantities of singlet oxygen is generated, thus killing bacteria. They are able to remain in the excited state for a longer period [15]. Water soluble phthalocyanine compounds have a particularly good action against micro-organisms in presence of oxygen and water and under irradiating with visible and / or infrared light as a result of photoactivation [16-18].

In our previous study [21], it was found that metallophthalocyanine (M: Zn) containing eugenol groups, was unsoluble in water, had an effective antibacterial activity against *S. aureus* bacteria on cotton fabric according to AATCC 100 standart.

Azo compounds constitute one of the largest classes of industrially synthesized organic compounds, exhibit a variety of interesting biological activities including antibacterial and pesticidal activities [22, 23]. Mkpenie *et al.* [23] reported that the presence of azo group, azo-2-naphthol, led to more than 60% antibacterial activity improvement.

A large number of reports on phthalocyanines substituted with varios azo group complexes appear in the literature [24-28].

In this study, the antibacterial effect of phthalocyanine structure containing both zinc metal ion and azo compound was investigated on cotton fiber fabric. Therefore, dyeability of cotton fiber with this water-soluble zinc phthalocyanine containing azo groups, leading to possible antibacterial property improvement, was examined. So, as a first step, the water-soluble zinc phthalocyanine containing azo groups was synthesized according to literature [24]. Then, cotton fiber fabric was cationized via modification with a cationic auxiliary. Afterwards, this cationized cotton fiber fabric was dyed with this synthesized Azo-ZnPc in the presence of sodium carbonate via exhaustion process. Finally, the colour fastness (to water, domestic and commercial laundering, rubbing, chlorinated water, perspiration, light), K/S, L, a*, b*, C*, h* values and antibacterial properties of the coloured cotton fiber fabric were investigated.

2. MATERIAL AND METHOD

2.1 Materials

The bleached, hydrophilic 100% cotton fiber fabric was in single jersey knit structure, 260g/m^2. 5g cationic cotton fabric was used for a dyeing bath of 1/10 ratio.

All used reagents and solvents were of analytical grade quality. Sulfanilic acid and phenol were obtained from Merck Chemical Company. Indosol E 50 Liq. was obtained from Clariant Chemicals and used as a cationic agent.

2.2 Methods

Synthesis of the green water-soluble zinc phthalocyanine containing azo groups was performed according to the procedure stated in the literature [24].

2.2.1 Synthesis of the water-soluble zinc phthalocyanine containing azo groups

4-Nitro–1,2-dicyanobenzene and 4-[(4-hydroxyphenyl) azo] benzene sodiumsulfonate **(1)** were prepared according to literature procedures [29, 30].

4-[(4-sodium sulfonatophenyl)azo 4'phenoxy)]-1,2-dicyanobenzene **(2)**:

Compound (**1**) (1550 mg, 5.58 mmol) and 4-Nitro –1,2-dicyanobenzene (960 mg, 5.5 mmol) were dissolved in dry DMSO (50 mL) and finely ground anhydrous Na_2CO_3 (1081 mg, 10.2 mmol) was added to this solution. Then, the reaction mixture was stirred at 60°C for 72 h. After reaction completed, the mixture was filtered off to remove undesired inorganic salts.

The filtrate was treated with ethanol to precipitate the product. The formed solid material was filtered off and washed with ethanol to obtain the pure product. NMR and elemental analysis validate highly pure product creation (Yield 1660 mg (74%); m.p. 170-172°C).

This compound was soluble in water, methanol and dimethylsulphoxide. FT - IRν_{max}/cm^{-1} 3088, 3037 (Ar-CH), 2243 (CN), 1585, 1571 (Ar), 1490 (N=N), 1221 (Ar - O -Ar), 1192 (O-S-O), 1122, 1036, 1010, 955, 919, 859, 825, 714, 694. ^{1}H NMR (DMSO - d_6) δ, ppm : 8.18 - 8.15 (1H, d, J = 8.8 Hz, ArCH), 8.04 - 8.02 (2H, d, J = 8.8 Hz, ArCH), 7.97 - 7.96 (1H, d, J = 2.4 Hz, ArCH), 7.88 - 7.81 (4H, m, ArCH), 7.59 - 7.56 (1H, dd, J= 2.4, 2.8 Hz, ArCH), 7.41 - 7.38 (2H, d, J = 8.8 Hz, ArCH).^{13}C NMR (DMSO-d_6) δ, ppm : 160.60, 157.12, 152.02, 151.35, 149.62, 136.90, 127.24, 125.49, 124.11, 123.64, 122.61, 121.20, 117,33 (CN), 116.32, 115.81, 109.55. Anal. Calcd. For $C_{20}H_{11}N_4NaO_4S$: C, 56.34; H, 2.60; N, 13.14. Found: C, 56.28; H, 2.58; N, 13.02.MS : m/z 403.02 [M – Na]$^-$.

Synthesis of tetra-substituted zinc phthalocyanine **(3)** :

Compound **2** (100 mg, 0.24 mmol), metal salt for zinc phthalocyanine ($Zn(CH_3COO)_2$,0.06mmol), amyl alcohol (15 mL), DMF (5 mL) and 2 - 3 drops DBU (1,8-diazabicyclo [5.4.0]undec-7-ene) were charged together into a round bottomed flask. The reaction flask was irradiated by a microwave apparatus at 800 W for 20 min. After cooling to the room temperature, formed solid product was filtered off and washed with ethanol. The obtained green product was purified by column chromatography (silica gel, MeOH - CH_2Cl_2, 10: 1). The synthesized phthalocyanine was soluble in water, methanol and DMSO. Yield 59 mg (37.8%), m.p. > 200°C. FTIRν_{max}/cm^{-1} 3060 (Ar-CH), 1646, 1590 (C=C), 1471 (N=N), 1228 (Ar-O-Ar), 1180 (O-S-O), 1116, 1030, 1006, 845, 704. Anal. Calcd. For $C_{80}H_{44}N_{16}Na_4O_{16}S_4Zn.3H_2O$: C, 52.47; H, 5.57; N, 12.24. Found: C, 52.53; H, 5.50; N, 12.26. UV/vis (DMSO): λ_{max} /nm 352, 613, 680.

2.2.2 Preparation of cationic cotton fabric

Dyeing and cationization processes were carried out in a laboratory dyeing machine with 1:10 liquor ratio according to the exhaustion technique. The cotton fabric needed to be processed with cationic agent prior to the dyeing application. The cationization agent (5%) was applied to cotton fiber fabric at pH 5 (via acetic acid) and 60°C for 20 minutes according to Figure 1. Then cotton fabric was washed with water and air-dried.

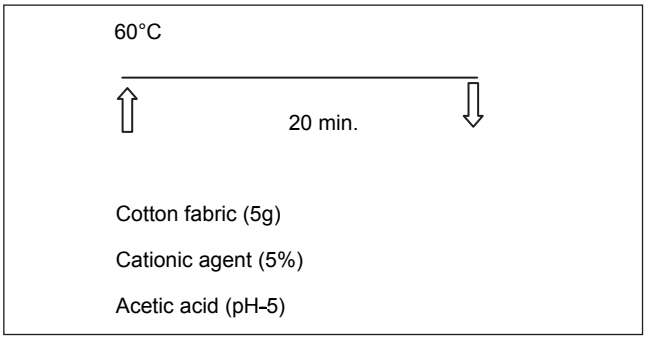


Figure 1. The cationization condition of cotton fabric.

2.2.3 Dyeing of cationic cotton fabric

After solubilization step (80°C, 45min.) of the dye with alkali, the water-soluble zinc phthalocyanine containing azo groups were applied to cationized cotton fiber fabrics at 80°C and pH 10 (via sodium carbonate) for 1% and 3% dye concentrations during 90 min. according to the dyeing procedure shown in Figure 2. After dyeing process, dyed cotton fabric was washed with water and neutralized using acetic acid. Finally, neutralized cotton fabric was again washed with water and air-dried for further testing.

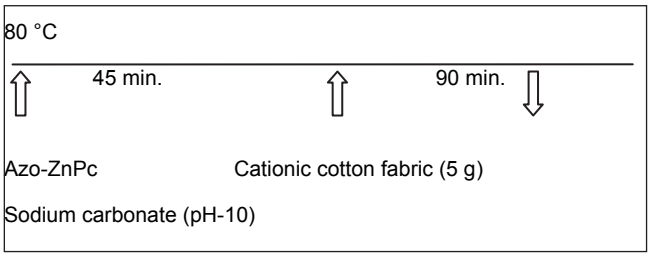


Figure 2. Dyeing procedure of cationized cotton fiber fabric.

2.2.4 Tests and Analyses

2.2.4.1 Characterization Analyses

For characterization, FT-IR spectra were recorded by Perkin-Elmer Spectrum 100 Infrared Spectrometer. UV/vis spectra were recorded by Perkin-Elmer UV/vis spectrometer. ^{1}H-NMR and ^{13}C-NMR studies were performed by Varian 400 FT-NMR. Elemental analyses were performed by the Instrumental Analysis Laboratory of the TUBİTAK Gebze Research Center. Mass spectra were performed by Thermo TSQ Quantum acces max. Microwave-assisted syntheses were carried out by using monomode CEM-Discover microwave apparatus.

Dyeing and cationization processes were carried out in a Termal Laboratory Dyeing Machine (Turkey). K/S values were determined by Hunterlab Ultrascan Pro VIS Spectrophotometer.

2.2.4.2 Fastness and antibacterial test methods

Cotton fabrics were tested according to ISO 105 - X12 for rubbing fastness, to TS EN ISO 105 - E01 for water fastness, to ISO 105 - C06 for domestic and commercial laundering fastness, to TS EN ISO 105-E04 for perspiration fastness, to TS EN ISO 105 - B02 for light fastness, to TS EN ISO 105-E03 for chlorinated water fastness.

Antibacterial activity of the cotton fabric was measured and evaluated according to AATCC 100 test method. The samples were tested against *S. aureus* (Gram positive) and *K. pneumoniae* (Gram negative) bacteria.

2.2.4.3 Color measurement

The samples were measured using an EasyMatch QC software of Hunterlab Ultrascan Pro color spectrophotometer attached to a personal computer. From

the reflectance value of dyed fabric at the max wavelength of absorbency (λ_{max}), the color strength (K/S) of the sample was calculated using the Kubelka–Munk equation (Eq. 1) :

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

Where R is the reflectance, K is absorbance and S is the scatteringcoefficient. The L, a*, b*, C* and h* values of the samples were also analyzed.

3. RESULTS AND DISCUSSION

3.1 Synthesis and characterization of water-soluble zinc phthalocyanine containing azo groups

Synthesis of green water soluble zinc phthalocyanine containing azo groups was performed according to procedure stated in the literature [24]. The synthesis route of the water soluble zinc phthalocyanine containing azo groups can be seen in Figure 3.

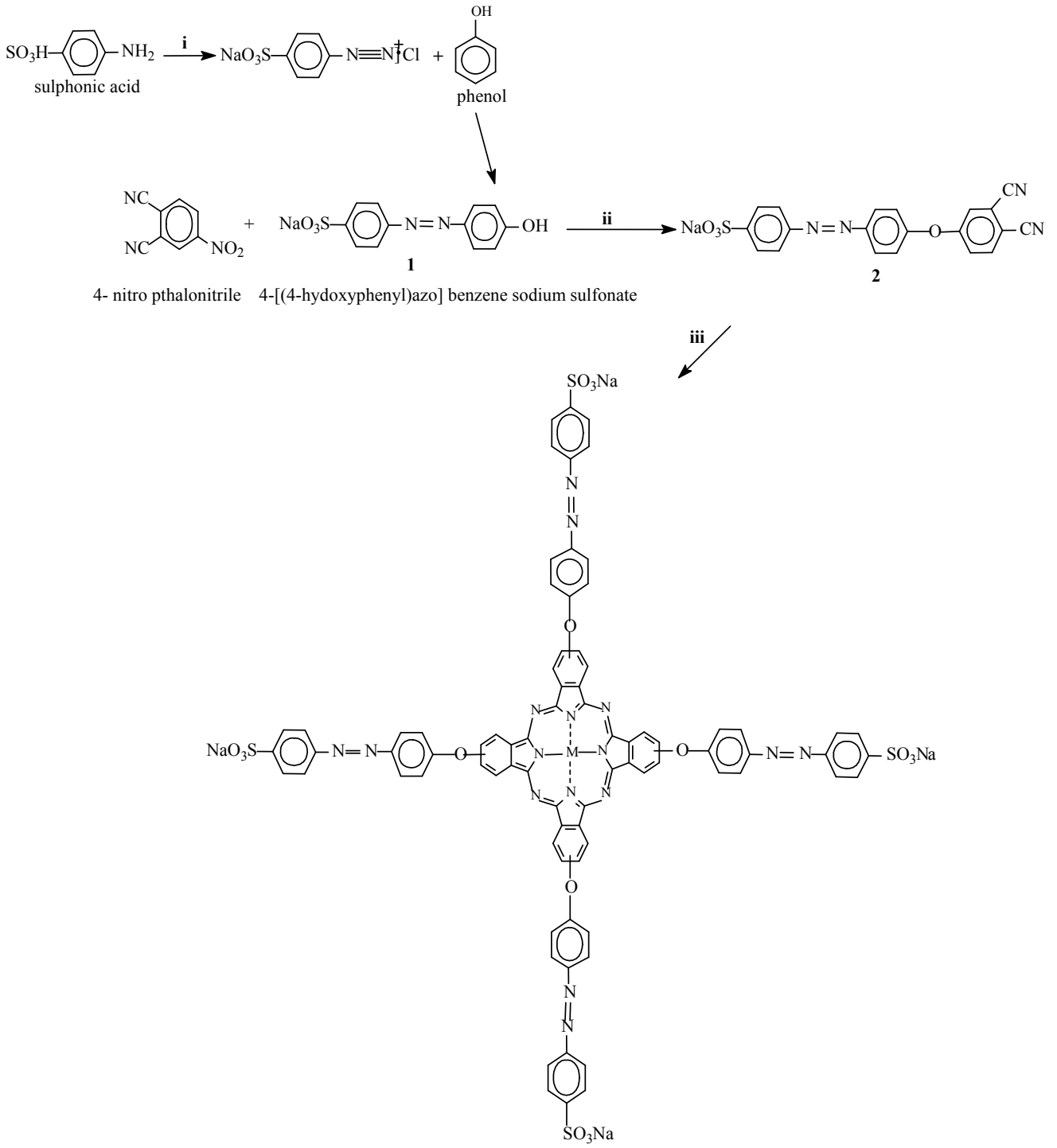


Figure 3. Structure of water-soluble zinc (M: Zn) phthalocyanine containing azo groups: (i) $NaNO_2$/HCl, 0 - 5 °C; (ii) 72 h, Na_2CO_3, DMSO, 60 °C; (iii) Microwave assisted synthesis method.

4-Nitro-1,2-dicyanobenzene is used to prepare phthalonitrile compounds. In order to obtain water soluble phthalocyanine containing azo groups, firstly 4-[(4-hydoxyphenyl) azo] benzene sodiumsulfonate (**1**) was prepared by the treatment of sulfanilic acid with phenol. The synthesis of phthalonitrile compound is the most important stage in these reaction series. For this purpose, compound (**2**) was synthesized by treating compound **(1)** with 4-nitro-1,2-dicyanobenzene, in DMSO using Na_2CO_3 as the base for nucleophilic aromatic substitution at 60°C for 72 h. Finally, zinc phthalocyanine was obtained from the starting phthalonitrile material and corresponding metal salt in amyl alcohol/DMF mixture for 20 min. by microwave assisted synthesis technique. All spectroscopic data and elemental analyses of compound (**1**)**,** (**2**) and the Azo-ZnPc exhibit good agreement with the previous findings [24]. Sodium sulfonate groups on molecule make the structure soluble in water. In the FT - IR spectrum, disappearance of the OH band at about 3300 cm^{-1} and the appearance of the CN band at 2243 cm^{-1} clearly indicate the formation of compounds **(2)**. FT - IR spectrum of the phthalocyanine clearly indicate the cyclotetramerization of the phthalonitrile derivative with the disappearance of the characteristic CN peaks at 2243 cm^{-1}.

The formation of compound **(2)** was certainly defined by the extinction of the OH peak at 10.42 ppm and appearance of the extra aromatic peaks two doublets at 8.18 - 8.15 and 7.97 - 7.96 ppm and one doublet-doublet at 7.59 - 7.56 for compound **2**, in it's ^1H NMR spectrum. The ^{13}C NMR spectrum of compounds **(2)** showed the presence of nitrile carbon atoms at 117.33 ppm.

The ^1H NMR and ^{13}C NMR spectra of zinc phthalocyanine were reasonably broader than the corresponding NMR signals in the phthalonitrile compound. It is probable that the signal broadening is due to the chemical exchange caused by aggregation–disaggregation equilibria.

Mass spectra (ESI) of compounds (**2)** provided a certain proof for their characterization. Mass spectra analyses were achieved using the negative-ion ESI, due to negative ion mode gave better results than positive mode for the compounds. Ionization took place in the methanol solution. Molecular ion peak of compound (**2)** was detected as expected. This peak was attributed to negative ion resulting from the loss of one Na^+ ion. Mass spectrum analysis approved the molecular mass of compound **(2)** m/z = 403.02 $[M\text{-}Na]^-$.

The best evidence for the phthalocyanine macrocylic is their UV/vis spectra in solutions. Metallophthalocyanine compounds have characteristic UV/vis spectra with two strong absorption peak regions, one of these peaks (B band) is in the UV region at about 200 – 350 nm, and the other peak (Q band) is in the visible region at 600 – 700 nm. The synthesized zinc phthalocyanine resulted in two strong absorption peaks in UV/vis spectrum, one of these peaks was at 352 nm (B band) and the other peak was at 680 nm (Q band) in DMSO, respectively. The UV/vis spectrum of zinc phthalocyanine is shown in Figure 4.

3.2 Colour strength and fastness values

Due to low solubility of the phthalocyanine in water, solubilization step (80°C, 45min.) is required in order to start dyeing process. Alkali media obtained with sodium carbonate (pH-10) was used for this purpose. After treating the phthalocyanine with alkali, sulfonic acid moieties change to sulfonates (negative ions) which are highly soluble in water.

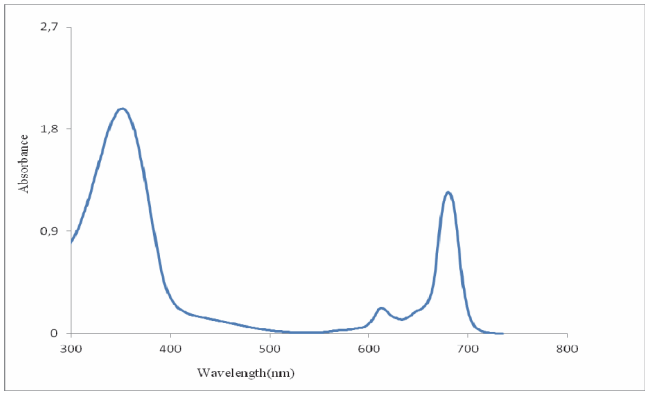


Figure 4. UV/vis spectrum of zinc phthalocyanine.

Dyeing (80°C, 90min) was not achieved without the cationization process because of the large aromatic dye structure. With the help of cationization process, the ionization of cotton fibers are becoming anionic in a wet medium, by the effect of affinity in dyeing, same colour tones obtained by using less amounts of dyestuffs. Pretreatment cationization process improved fabrics dyeabilities. Water soluble dye linked with cationized cotton in alkali media due to the electrostatic interactions between sulfo groups of the dye and cationic groups of cotton fiber. The formed electrostatic interactions improved affinities so it's application method likes direct dye class.

After dyeing with the new water soluble zinc phthalocyanine, cotton fabric exhibited uniformly green coloured surface (Table 1).

The a* values, as shown in Table 1, indicate that all samples are in greener tone. The b* values show that the samples are yellower. The L* values indicate that the samples have lighter shades (L value between black = 0 and white = 100). When the concentration of the dye is increased from 1% to 3%, the L* value decreases slightly; however, K/S value increases and results in relatively darker shade. The hue values are in 90°-180°, so they exhibit yellowish green tone. When the concentration of the dye is increased from 1% to 3%, the hue value increases, so the result is greener. Chroma or colour brilliance value shows distance from grey, the obtained values are almost constant.

Colour fastness results at 1% and 3% dye concentrations were given in Table 3-5.The colour fastness properties were measured in a scale of 1-5 (very poor, poor, fair, good and very good). Water, washing, dry rubbing and perspiration fastness values of cationized and then dyed cotton fiber fabrics (at 1 % and 3 % dye concentrations) were in the range of 4/5 and 5 gray scale ratings leading to high, commercially acceptable wet fastness levels. The dyed cotton fabric exhibited very poor light fastness level with only grade 1 according to the wool scale rating at 1% dye concentration. The reason of the observed poor light fastness performance might be due to the substituents on

metallophthalocyanine. The light fastness value increased slightly (grade from 1 to 2) when the concentration of dye was increased from 1% to 3%. Moderate wet rubbing (grade 3-4 for both 1%, 3% dye concentrations) and fair chlorinated water fastness results (grade 3 for 1%, grade 2 for 3 % dye concentration, at light conditions) were observed.

Table 1. K/S, L, a*, b*, C* (chroma) and h* (hue) values of the dyed fabrics at 1% and 3% dye concentrations.

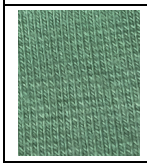
Colour Produced On Cotton Fabric	% Dye Concentration	K/S λ_{max}, 400nm	L*	a*	b*	C*	h*
% Dye Concentration 1 3	1	1.24	71,01	-13,51	8,99	16,23	146,37
 	3	1.62	66,35	-16,61	6,14	17,71	159,72

Table 2. Water fastness properties of samples dyed with new water soluble zinc phthalocyanine at 1% and 3% dye concentrations (TS EN ISO 105-E01).

Colour fastness to water	% Dye Concentration	Colour change	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
	1	4-5	5	5	5	5	5	5
	3	4-5	5	5	5	5	5	5

Table 3. Domestic and commercial laundering fastness properties of samples dyed with new water soluble zinc phthalocyanine at 1% and 3% dye concentrations (ISO 105-C06**,** at 40 ºC).

Colour fastness to domestic and commercial laundering	% Dye Concentration	Colour change	Staining					
			Acetate	Cotton	Nylon	Polyester	Acrylic	Wool
	1	4-5	4-5	4-5	4-5	4-5	4-5	5
	3	4-5	4-5	4-5	4-5	4-5	4-5	5

Table 4. Perspiration fastness properties of samples dyed with new water soluble zinc phthalocyanine at 1% and 3% dye concentrations (TS EN ISO 105-E04).

Colour fastness to perspiration	% Dye Concentration		Colour change	Staining					
				Acetate	Cotton	Nylon	Polyester	Acrylic	ool
	1	Acidic	4-5	4-5	4-5	4-5	4-5	4-5	5
		Alkaline	4-5	4-5	4-5	4-5	4-5	4-5	
	3	Acidic	4-5	4-5	4-5	4-5	4-5	4-5	5
		Alkaline	4-5	4-5	4-5	4-5	4-5	4-5	

Table 5. Light fastness (TS EN ISO 105-B02), rubbing fastness (TS EN ISO 105-X12), chlorinated water fastness (swimming-pool water) (TS EN ISO 105-E03) properties of samples dyed with new water soluble zinc phthalocyanine at 1% and 3% dye concentrations.

% Dye Concentration	Light Fastness	Rubbing Fastness		Colour fastness to chlorinated water	
				Colour Change	
1	1	Wet	Dry	Hard Conditions	Light Conditions
		3-4	4-5	1-2	3
3	2	3- 4	4-5	1-2	2

3.3 Antibacterial activity

Photosensitizing properties of phthalocyanines and their effects to actibacterial action on fabric were generally determined by exposing to light under infrared or visible light lamp in literature [16-18]. In our study, antibacterial activity of the cotton fabric was measured and evaluated according to AATCC 100 test methods, not applied special irradiation procedure. The samples were tested against *S. aureus*

(Gram positive) and *K. pneumoniae* (Gram negative) bacteria.

"Antibacterial finishes on textile materials" AATCC 100 provides a quantitative procedure for the evaluation of degree of antibacterial activity. Samples of test and control textile materials are inoculated with the test organisms. The method frequently is performed with *Staphylococcus aureus* and *Klebsiella pneumoniae*, but can be performed with many others. After inoculation, the bacteria were eluted from the swatches by shaking in known amounts of neutralizing solution. The number of bacteria present in this liquid is determined, and the percentage reduction by the treated specimen is calculated (Eq. 2).

$$\text{Reduction \% (CFU/ml)} = [(B-A) / B] \times 100 \quad (2)$$

where A are the surviving cells (CFU/ml) for the flasks containing the treated substrate (the Azo-ZnPc dyed cotton fabric) after the specified contact time and B are "0" contact time CFU/ml for the flasks used to determine A before the addition of the treated substrate.

Antibacterial activity results are given in Table 6. It was observed that the dyed fabric had an effective antibacterial action to pathogenic *S. aureus* and *K. pneumoniae* bacteria (approximately 100%) at 1% dye concentration. *S. aureus* is a type of Gram – positive bacteria that can cause numerous infections, including impetigo, scalded skin syndrome, folliculitis, furuncle, carbuncle, osteomyelitis, septic arthritis, endocarditis, toxic shock syndrome, pneumonia, thrombophlebitis, deep tissue abscess and infection [31]. *K. pneumoniae* is a type of Gram-negative bacteria that can cause different types of healthcare-associated infections, including pneumonia, bloodstream infections, wound or surgical site infections, and meningitis. Patients whose care requires devices like ventilators (breathing machines) or intravenous (vein) catheters, and patients who are taking long courses of certain antibiotics are at high risk for *Klebsiella* infections [32]. These bacteria can be spread through person - to - person contact (for example, from patient to patient via the contaminated hands of healthcare personnel, or other persons) or, less commonly, by contamination of the environment.

In literature [19, 20], it was reported that several porphyrins and phthalocyanines have been shown to display a potent photocytotoxic effect against Gram-positive bacteria but Gram-negative bacteria are resistant to bacterial photosensitization with anionic or neutral porphyrin and phthalocyanine photosensitizers because the outer membrane prevents the uptake of these compounds into the cell. Only with the advent of cationic phthalocyanine and porphyrin photosensitizers has this resistance been overcome. In our study, the antibacterial activity results showed that this dye, anionic character in water media, was very effective on the both of Gram-positive and Gram-negative bacteria.

It is thought that effective antibacterial action of the dye on cotton fabric can be ensured by zinc metal ion and azo groups presence simultaneously in one phthalocyanine dye structure. It may be said that antibacterial effect of azo groups are markedly higher than eugenol groups on zinc phthalocyanine when compared with the literature [21]. It can be said that antibacterial activity of zinc phthalocyanine was changed with substituent group type. It was estimated that the more dye concentration on fabric cause the more antibacterial action.

4. CONCLUSIONS

It is known that azo groups and metal ions have antibacterial abilities by themselves but in this work, for the first time in the literature, it was demonstrated that water soluble zinc phthalocyanine containing azo groups exhibited effective antibacterial activity, rated as 99.99 %, 99.74 % against *S. aureus* and *K. pneumoniae* bacteria on cotton fabric, respectively. This new dye was used for textile coloration for the first time in this study. Dyeing properties, colour fastnesses (to light, water, perspiration, chlorinated water, rubbing), color strength and the antibacterial activities of cotton fabric were investigated. Uniformly even green coloured dyeing was achieved with exhaustion process by electrostatic interactions between sulfo groups of dye and cationic groups of cotton. Pretreatment cationiation process ensured fabrics dyeability.

High antibacterial protection is achieved only via coloration with this new dye without any additional antibacterial finishing process. Despite of poor light fastness value, good water, washing, dry rubbing and perspiration fastness results and moderate wet rubbing, chlorinated water fastness results were obtained at 1% and 3% dye concentrations so it can ensure variety uses of the dyed textile. In the future, this green coloured antibacterial fabric can be used in military, healthcare, work/uniforms, domestic products and sports apparel, especially in medical textiles such as hospital linens, barrier fabrics, protective clothing, bandages, wound dressing…etc. for preventing *S. aureus* and *K. pneumoniae* bacteria which may lead to numerous infections on human.

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Table 6. Antibacterial activity test results of cotton fabric dyed with water soluble zinc phthalocyanine containing azo groups at 1% dye concentration.

Microorganisms	The presence of propagation on the surface	Reducing percent of microorganism %
S. aureus (Gr +)	Not seen	99.99
K. pneumoniae (Gr -)	Not seen	99.74

REFERENCES

1. Garcia J., Gonzalez A., Gouloumis A., 1998,“Phthalocyanines and Related Compounds: Subunits for the Preparation of Molecular Materials”, *Tr. J. Of Chemistry*, 1998: 22 (1), p:23-31.
2. “Copper Phthalocyanines”, http://www.pcimag.com/articles/copper-phthalocyanines, (Access date: 21 February 2014)
3. Han K-J., Kay K-Y., 2005, ‘‘Synthesis and Photoresponsive Properties of Cu – Phthalocyanine With Azobenzene Groups’’, *Bull. Korean Chem. Soc.,* 2005: 26(8), p: 1274 – 1276.
4. Kumar G. A., Thomas J., George N., 2000, ‘‘Physical And Optical Properties Of Phthalocyanine Doped İnorganic Glasses’’, *Journal Of Materials Science*, 2000: 35, p: 2539 – 2542.
5. Hamuryudan E., Akkurt B., 2008, “Enhancement Of Solubility Via Esterification: Synthesis and Characterization Of Octakis (Ester)-Substituted Phthalocyanines”, *Dyes and Pigments*, 2008: 79, p:153-158.
6. Christie R. M., 2001, ‘‘Chapter 5: Phthalocyanines’’, *Colour Chemistry*, The Royal Society Of Chemistry, p: 1-201, ISBN 0-85404-573-2
7. Wöhrle D., Schnurpfeil G., Makarov S. G., 2012, ‘‘Practical Applications Of Phthalocyanines – From Dyes And Pigments To Materials For Optical, Electronic And Photo – Electronic Devices’’, *Macroheterocycles*, 2012: 5(3), p: 191 – 202, DOI: 10.6060/mhc2012.120990w
8. Bamfield P., Hutchings M G, 2010, ‘‘Chapter 2: Phenomena Involving The Absorption And Reflectance Of Light’’, *Chromic Phenomena: Technological Applications Of Colour Chemistry*, Royal Society of Chemistry, 2nd Edition, UK, p:185, ISBN: 978-1-84755-868-8.
9. Joshi M., Ali S. W., Purwar R., 2009, ‘‘Ecofriendly Antimicrobial Finishing Of Textiles Using Bioactive Agents Based On Natural Products’’, *Indian Journal Of Fibre & Textile Research*, 2009: 34, p: 295 – 304.
10. Yasuyuki M., Kunihiro K., Kurissery S., 2010, “Antibacterial Properties Of Nine Pure Metals: A Laboratory Study Using Staphylococcus Aureus and Escherichia Coli”, Biofouling: The Journal Of Bioadhesion and Biofilm Research, 2010: 26(7), p:851-858, DOI: 10.1080/08927014.2010.527000
11. Rizzotto M., 2012, “Chapter 5: Metal Complexes As Antimicrobial Agents”, *A Search For Antibacterial Agents*, Bobbarala V. (Ed.), InTech, p:73, ISBN : 978-953-51-0724-8, DOI: 10.5772/45651, http://www.intechopen.com/books/a-search-for-antibacterial-agents/metal-complexes-as-antimicrobial-agents , (Access date: 02 September 2014)
12. Chang E. L., Simmers C., Knight D. A., 2010, “Cobalt Complexes As Antiviral And Antibacterial Agents”, *Pharmaceuticals*, 2010:3, p:1711-1728, DOI: 10.3390/ph3061711
13. Landage S. M., Wasif A. I., 2012, “Nanosilver-An Efective Antimicrobial Agent For Finishing Of Textiles”, *International Journal of Engineering Sciences & Emerging Technologies*, 2012: 4(1), p:66-78, ISSN: 2231 -6604
14. Rajendran R., Balakumar C., Ahammed H. A. M., 2010, ‘‘Use Of Zinc Oxide Nano Particles For Production Of Antimicrobial Textiles’’, *International Journal Of Engineering, Science and Technology*, 2010: 2(1), p:202 -208.
15. Ryskova L., Buchta V., Karaskova M., 2013, “In Vitro Antimicrobial Activity of Light-Activated Phthalocyanines”, *Central European Journal of Biology*, 2013:8(2), pp168-177.
16. Polony R, Reinert G, Hölzle G, 1985, *United States Patent*, Patent Number: 4,530,924
17. Hölzle G, Reinert G, Polony R, 1984, *United States Patent*, Patent Number:4, 456,452
18. Polony R, Reinert G, Hölzle G, 1982, *United States Patent*, Patent Number: 4,318,883
19. Minnock A., Vernon D. I., Schofield J., 1996, “Photoinactivation of bacteria. Use of a Cationic Water-Soluble Zinc Phthalocyanine to Photoinactivate both Gram-negative and Gram-positive Bacteria”, *Journal of Photochemistry and Photobiology B: Biology*, 1996:32(3) , pp159-164.
20. Minnock A., Vernon D. I., Schofield J., 2000, “Mechanism of Uptake of a Cationic Water-Soluble Pyridinium Zinc Phthalocyanine across the Outer Membrane of *Escherichia coli*”, *Antimicrobial Agents and Chemotherapy*, 2000:44 (3),pp 522-527.
21. Özgüney A., Kantar C., Saral P., 2013, ‘‘Investigation Of Fastness Properties And Antibacterial Effect Of Metallophthalocyanine (M : Zn) Containing Eugenol Printed On Cotton Fabric’’, *Tekstil ve Konfeksiyon*, 2013 : 23(2), p: 261 – 266.
22. Hamid H. M., Zeinab N. M., Istabraq M. A., 2011, ‘‘Synthesis And Studies The Biological Activity Of New Azo Compounds’’, *Journal Of Kerbala University*, 2011: 9(3), p:75 -83.
23. Mkpenie V., Ebong G., Obot I. B., 2008, ‘‘Evaluation Of The Effect Of Azo Group On The Biological Activity Of 1-(4-Methylphenylazo)-2-naphthol’’, *E – Journal Of Chemistry*, 2008: 5(3), p: 431 – 434, ISSN : 0973 – 4945
24. Kantar C., Atacı E., Şaşmaz S., 2014, “Water Soluble Phthalocyanines Containing Azo Dye; Microwave Assisted Synthesis And Photochemical Properties Of ZnPcs”, *Turkish Journal of Chemistry*, DOI: 10.3906/kim-1404-35.
25. Li Y-F., Li S-L., Jiang K. J., 2004, “Synthesis and Spectral Property of Novel Phthalocyanines Substituted with Four Azo Group Moieties on Periphery of Phthalocyanine Ring”, *Chemistry Letters*, 2004: 33, pp:1450-1451.
26. Yazıcı A., Ateş D., Bekaroğlu Ö., 2006, “Synthesis and Charecterization of Novel Azo-bridged Zn(II) and Co (II) Bisphthalocyanines”, *Journal of Porphyrins and Phthalocyanines*, 2006: 10(9), p1140.
27. Şaşmaz S., Kaya Kantar G., Hacıalioğlu E., 2014, “Synthesis and Properties of Phthalocyanines Containing A New Triazol-5-one Moieties, *El-Cezerî Journal of Science and Engineering*, 2014:1(11), p:1-6.
28. Àlvarez Micó X., Vagin S. I., Subramanian L. R.,2005, “New Unsymmetrical Zinc-Phthalocyanine Conjugated with One Azo-Dye Moiety: Synthesis via Opening the Fused Triazole Ring and Spectral Properties” *European Journal of Organic Chemistry*, 2005: 2005 (20), p:4328-4337, DOI: 10.1002/ejoc.200500237.
29. Young J. G., Onyebuagu W., 1990, “Synthesis and Characterization of Di-disubstituted Phthalocyanines”, *J. Org. Chem.,* 1990:55(7), p:2155-2159.
30. Ojala W. H., Sudbeck E. A., Lu L. K., 1996, “Complexes of Lysine, Histidine, and Arginine with Sulfonated Azo Dyes: Model Systems for Understanding the Biomolecular Recognition of Glycosaminoglycans by Proteins”, *J. Am. Chem. Soc.,* 1996: 118 (9), p: 2131-2142.
31. ‘‘Staphylococcus Aureus Infection’’ http://emedicine.medscape.com/article/971358-overview, (Access Date: 26 February 2014).
32. ‘‘*Klebsiella Pneumoniae* in Healthcare Settings’’, http://www.cdc.gov/HAI/organisms/klebsiella/klebsiella.html, (Access Date: 26 February 2014).