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Review

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Antimicrobial dyes based on heterocyclic and/or homocyclic systems for dyeing and textile finishing

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ABSTRACT

This review article deals with the antimicrobial finishing of textiles with antimicrobial dyes based on heterocyclic / homocyclic systems also deals with the Antimicrobial Activity, Structural Features of Antimicrobial Functional Dyes, Requirements for Antimicrobial Finishing and various methods that sued for Evaluation of Antimicrobial Efficacy of these dyes (qualitative and quantitative). This review article also describes the major antimicrobial activity of dyes based on heterocyclic / homocyclic systems. Keeping in mind the multitude of existing systems, different dyes is classified as natural, direct, cationic, reactive and disperse dyes. In addition, this article review illustrates the use of these dyes for dyeing as well as antimicrobial textile finishing.

KEYWORDS

Antimicrobial dyes;
Heterocyclic systems;
Homocyclic systems;
Dyeing and textile finishing;
Antimicrobial textiles.

INTRODUCTION

Textiles recognized as media to support the growth of microorganisms such as bacteria and fungi. These microorganisms are found in the environment and may multiply quickly when basic requirements, such as moisture, nutrients and temperature are met. Almost synthetic fibers, owing to their high hydrophobicity, are more resistant to attacks by microorganisms than natural fibers. Proteins in keratinous fibers and carbohydrates in cotton may act as nutrients and energy sources under certain conditions. Soil, dust, solutes from sweat and some textile finishes may also be nutrient sources for microorganisms[1,2].

The growth of microorganisms on textiles not only inflicts a range of unwanted effects on the textile itself but also on the wearer. These effects include the generation of unpleasant odor, stains and discoloration in the fabric, a reduction in fabric mechanical strength and an increased likelihood of contamination. For these reasons, it is highly desirable that the growth of microbes on textiles be minimized during their use and storage.

There is also a broader market for antimicrobial fibers, for instance, in outdoor textiles, air filters, automotive textiles, domestic home furnishings and medical textiles. This high demand, in turn, has stimulated intensive research and development[1,2].

Producing functional dyes with special finishing capabilities promote currently in an area of active research especially in the field of textile applications. This review article shall discuss a variety of functional dyes that posse's biological activity[3-5]. However, there has been a growing need to develop finishes for textile materials that may offer improved protection to the users from microbes (bacteria, mould or fungi) which cause numerous problems. Textile materials and clothing are known to be susceptible to microbial attack, as these provide large surface area and absorb moisture required for microbial growth[6]. Natural fibres have protein (keratin), cellulose etc., that provide basic requirements such as moisture, oxygen, nutrients and temperature for bacterial growth and multiplication. This often leads to undesrable odour, dermal infection, product deterioration, allergic responses and other related diseases[7]. This necessitates the development of clothing that may provide a desired antimicrobial effect.

A variety of antimicrobial textile materials are reported employing different approaches as development of chitosan treated wool fabrics[3], antimicrobial nylon fiber by attaching a phosphate glass as an antimicrobial agent[8], surface coating by trialkoxysilyl quaternary ammonium salt, antibacterial fiber by graft polymerization of cellulosic fiber with polyvinylpyrrolidone, by treatment with potassium iodide solution, micro-encapsulation or insolubilization of chemical reagents in/on fiber such as nitro compounds on acrylic, nylon, polypropylene and polyethylene fiber. These recent approaches use synthetic non-biodegradable chemical compounds, that cause environmental and health concerns. As an alternate approach, if some special dyes having antimicrobial activities without significantly affecting their dyeing properties, the textile dyeing and antimicrobial finishing may be unified into one process. With these approaches in mind, some studies have been conducted so far to check the antimicrobial activity of these dyes when applied on textile materials. This article addresses the viability of using textile dyes that represent the antimicrobial dyes with high performance dyeing and antimicrobial textile finishing.

REQUIREMENTS FOR ANTIMICROBIAL FINISHING

In order to obtain the greatest benefit, an ideal antimicrobial treatment of textiles should satisfy a several requirements[1,2,9].

- It should be effective against a broad spectrum of bacterial and fungal species, but at the same time exhibits low toxicity to consumers, e.g. does not cause toxicity, allergy or irritation to the user.
- The finishing should be durable to laundering, dry cleaning and hot pressing, e.g. textile products subjected to repeated washing during their life.
- The finishing should not negatively affect the quality (e.g. physical strength and handle) or appearance of the textile.
- The finishing should preferably be compatible with textile chemical processes such as dyeing, be cost effective and not produce harmful substances to the manufacturer and the environment.
- Antimicrobial finishing of textiles should not kill the resident flora of nonpathogenic bacteria on the skin of the wearer[10].

STRUCTURAL FEATURES OF ANTIMICROBIAL FUNCTIONAL DYES

Functional dyes and colorants are compounds whose electronic structures can absorb electromagnetic radiation in the visible range (380-780 nm); additional properties other than color can be defined as functions. Based on this definition, Infrared dyes, laser dyes and voltage sensitive dyes fall within the category of functional dyes[11].

Functional dyes and colorants are useful for imparting a functional property to a textile such as antimicrobial, anti-static, softening, water repellent, fire-resistant, soil-repellent, anti-UV, and other chemical properties as well as a combination of two or more properties thereof.

Antimicrobial dyes have the ability to kill at least some types of microorganisms (called bactericidal) or to inhibit the growth or reproduction of these organisms (called bacteriostatic)[12].

Textile materials are excellent media for growing of microorganisms such as, *Staphylococcus aurues, Escherichia coli, Aspergillus niger etc.* An environmental concern, to the public, owing to increasing of the cross transmission of diseases in hospitals and unhealthy indoor air quality in working areas partially or completely caused contaminated textiles. Body odour and dermal infections, caused by microorganisms, are hygienic concern as well.

Fabrics possessing inherent antimicrobial functions are expect to be able to eliminate these concerns[13]. Clothing and textile materials are carriers of microorganisms such as pathogenic bacteria, odor-generating bacteria, and mold fungi, because of the adhesion of these microorganisms on fabric surfaces. The spread of HIV and hepatitis viruses by contact of contaminated materials has created increased pressure for protection of personal with functional clothing and materials[14].

Therefore, medical use and institutional use apparel materials and clothing such as surgeons' gowns, patient drapes, nurses' clothing, carpeting and bedding materials, lining sheets and towels, and worker uniforms are necessary to achieve antibacterial functions[15].

Textiles dyed with antimicrobial dyes have microbiocidal (i.e. antimicrobial), activity against a broad spectrum of pathogenic microorganism *e.g.* gram-positive bacteria (e.g. Staphylococcus *aurous*) and gram-negative bacteria (Escherichia *coli*). Fibers with microbicidal properties are intended for use particularly in the medical sector, for example for women's wear, underwear, socks and other hygienic purposes such as upholsteries.

ANTIMICROBIAL ACTIVITY

Microbes and application of some antimicrobial dyes

Microbes are the tiniest creatures not seen by the naked eye. Each include a variety of microorganisms as bacteria, fungi, algae and viruses. Bacteria are unicellular organisms, that growing rapidly under warmth and moisture. Further, subdivisions in the bacteria family are Gram-positive bacteria e.g. (S. *aureus*), Gram-negative bacteria e.g. (E.*Coli)* or spore bearing and non-spore bearing type. Some specific types of bacteria are pathogenic and cause cross infection. Fungi, molds or mildew are complex organisms with slow growth rate. Each stain the fabric and deteriorate the performance properties of the fabrics. Fungi are active at a pH level of 6.5. Algae are typical microorganisms that are either fungal or bacterial. Algae require continuous sources of water and sunlight for growth and develop darker stains on the fabrics. Algae are active in the pH range of 7.0-8.0. Dust mites are eight legged creatures and occupy the household textiles such as blankets bed linen, pillows, mattresses and carpets. The dust mite's fees on human skin cells and liberated waste products can cause allergic reaction and respiratory disorders[16].

Many investigators use many kinds of dyes for management of microbes on textile as shown in TABLE 1.

Evaluation of antimicrobial efficacy

A number of test methods have been developed to determine the efficacy of antimicrobial textiles[62,63]. The bacterial species Staphylococcus aureus (Gram positive) and Klebsiella pneumonia (Gram negative) are recommended in almost test methods. These two species are potentially pathogenic and therefore require proper physical containment facilities for handling (e.g. a bio-safety cabinet). Many studies have used the innocuous Escherichia coli (Gram negative) as a test microorganism that can be cultured and handled in a standard laboratory with minimal health risk. These methods are:

Broth dilution tests

One of the earliest antimicrobial susceptibility testing methods was the macro broth or tube-dilution method[64-66]. This procedure involved preparing two-fold dilutions of antimicrobial material (eg, 1, 2, 4, 8, and 16 mg/mL) in a liquid growth medium dispensed in test tubes[64-67]. The antimicrobial containing tubes inoculated with a standardized bacterial suspension. Following overnight incubation at 37°C, the tubes were examined for visible bacterial growth as evidenced by turbidity. The lowest concentration of antimicrobial that prevented growth represented the minimal inhibitory concentration (MIC). The advantage of this technique was the generation of a quantitative result. The disadvantages of the macro dilution method were the tedious, manual task of preparing the antimicrobial solutions for each test, the possibility of errors in preparation of the antimicrobial solutions, and the relatively large amount of reagents and space required for each test. The miniaturization and mechanization of the test by use of small, disposable, plastic 'micro dilution' trays (Figure 1) has made broth dilution testing practical and popular. Micro dilution panels are typically prepared using dispensing instruments that aliquot precise volume of pre-weighed and diluted antimicrobial in broth into the individual wells of trays from large volume vessels. MICs are determined using a manual or automated viewing device for inspection of each of the panel wells for growth[67]. The advantages of the micro dilution procedure include the generation of MICs, the reproducibility and convenience of having prepared panels, and the economy of reagents and space that occurs owing to the miniaturization of the test. The main disadvantage of the micro dilution method is some inflexibility of drug selections available in standard commercial panels.

TABLE 1 : Some types of antimicrobial dyes and their effects on some harmful microorganisms

Dye	Microorganisms	References
Natural dyes	Gram-negative bacteria Escherichia coli (E. coli), Bacillus subtilis (B. subtilis), Klebsiella pneumoniae (K. pneumoniae), Proteus vulgaris (P. vulgaris), Pseudomonas aeruginosa (P. aeruginosa).	[17-28]
Direct dyes	Gram-positive bacteria Staphylococcus aurues (S. aureus), Staphylococcus pyogenes (S. pyogenes), Gram-negative bacteria (E.coli), (P. aeruginosa), (P. vulgaris).	[29 and 30]
Cationic dyes	Gram negative bacteria E. coli, K. pneumonia, P. vulgaris, Pseudomonas pyocynans (P. pyocynans), Salmonella typhi (S. typhi), Vibrio cholerae (V. cholera) Gram positive bacteria S. aurues, S. Pyogens, Staphylococcus epidermidis (S. epidermidis), Corynebacterium, diphtheroids	[31-42]
Reactive dyes continued	Gram-negative bacteria E. coli, P. aeruginosa Gram-positive bacteria S. aureus, S. pyogenes, C. albicans, A. niger, A. clavatus Fungi Aspergillus niger, Penicillium species	[43-47]
Disperse dyes	Gram negative bacteria E. coli, B. subtilis, P.vulgaris, Salmonella sp., Pseudomonas sp., Rhodococci Gram positive bacteria S. aureus, Fungi Aspergillus niger, Penicillium species	[48-61]

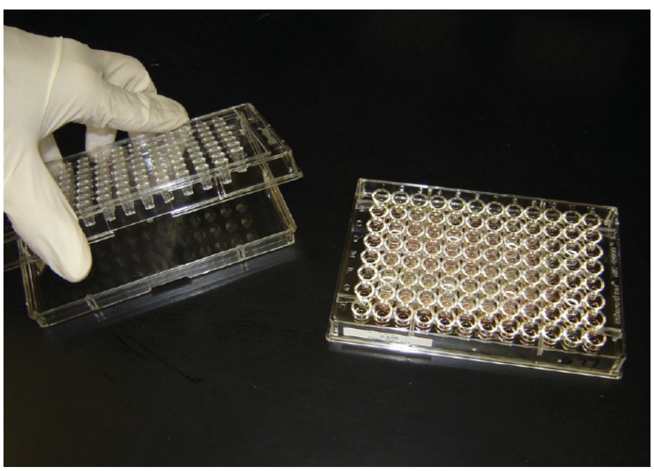


Figure 1 : A broth micro dilution susceptibility panel containing 98 reagent wells and a disposable tray inoculator

Antimicrobial gradient method (E-test)

The antimicrobial gradient diffusion method uses the principle of establishment of an antimicrobial concentration gradient in an agar medium as a means of determining susceptibility as shown in Figure 2. It employs thin plastic test strips that impregnated on the underside with a dried antimicrobial concentration gradient and are marked on the upper surface with a concentration scale. As many as 5 or 6 strips placed in a radial fashion on the surface of an appropriate 150-mm agar plate that has been inoculated with a standardized organism suspension as that used in a disk diffusion test. After overnight incubation, the tests are read by viewing the strips from the top of the plate. The MIC is determined

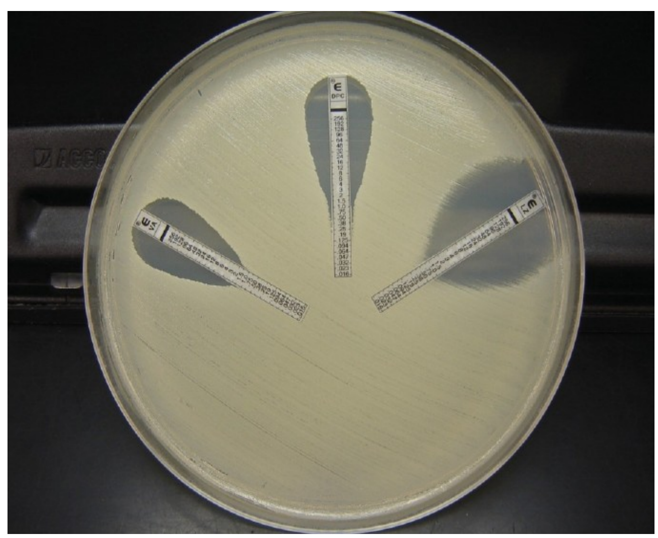


Figure 2 : E-test gradient diffusion method with some antimicrobials. The minimum inhibitory concentration of each agent is determined by the intersection of the organism growth with the strip as measured using the scale inscribed on the strip.

by the intersection of the lower part of the ellipse shaped growth inhibition area with the test strip. Generally, E-test results have correlated well with MICs generated by broth or agar dilution methods[68-72].

Disk diffusion test

The disk diffusion method[66,67,73,74] is simple, practical, and well standardized. The test done by applying a bacterial inoculum to the surface of a large (150 mm diameter) Mueller-Hinton agar plate. Up to 12 commercially prepared, fixed concentrations, paper antimicrobial disks placed on the inoculated agar surface (Figure 3). Plates incubated for 24 h at 37^{0}C before determination of results. The zones of growth inhibition around each of the antimicrobial disks measured to the nearest millimeter. The diameter of the zone related to the susceptibility of the isolate and to the diffusion rate of the material through the agar medium. The results of the disk diffusion test are ‘qualitative,’ in that a category of susceptibility (ie, susceptible, intermediate, or resistant) is derived from the test rather than an MIC. The advantages of the disk method are the test simplicity that does not require any special equipment, the provision of categorical results easily interpreted by all clinicians, and flexibility in selection of disks for testing. The disadvantages of the disk test are the lack of mechanization or automation of the test.

Suspension test

This test provide quantitative values on the antimicrobial finishing, but is more time-consuming more than agar diffusion test. Typically, a small volume (e.g. 1 ml) of bacterial inoculum in a growth media is fully absorbed

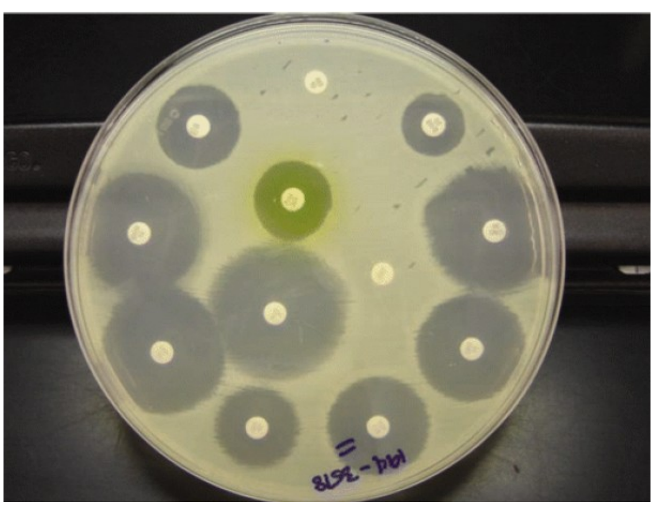


Figure 3 : Plates showing antimicrobial activity by agar diffusion method.

into dyed fabric samples of appropriate size without leaving any free liquid. This ensures intimate the contact between the dyed fabric and the bacteria. After incubating the inoculated fabrics in sealed jars at 37°C for up to 24 h, the bacteria in the fabric are eluted and the total number is determined by serial dilution and plating on nutrient agar plates. Antimicrobial activity, expressed as percentage of reduction, calculated by comparing the size of the initial population and that following the incubation. Appropriate controls, e.g. samples that have gone through the same process except the antimicrobial finishing, should be included in each experiment to ascertain that the observed decrease in bacterial number is truly due to the antimicrobial finishing[66].

ANTIMICROBIAL TEXTILE DYES

Natural dyes

Many of the plants are used for dye extraction are classified as medicinal, and some of these have remarkable antimicrobial activity. *Punica granatum* and many other common natural dyes are reported as potent antimicrobial agents because of the presence of a large amount of tannins. Several other sources of plant dyes are rich in naphthoquinones such as lawsone from henna, juglone from walnut and lapachol from alkannet are reported to exhibit antibacterial and antifungal activity[17,63].

Dyeing with natural products has attracted almost attention owing to their additional functions such as antibacterial, antifungal and deodorizing effects that some of natural matters may provide to fibers via dyeing. Such application of them to fibers may be a rather functional dyeing technology that has many advantages both economically and environmentally[19]. Furthermore, it could meet the growing consumer need for safe and healthy life and the global awareness of eco-friendly industrial process. For these reasons, many efforts made to investigate traditionally used natural dyes in term of their dye ability including dyeing procedures, shade of dyed fabrics, fastness properties and furthermore their hygienic functions on fabrics[18,20,21].

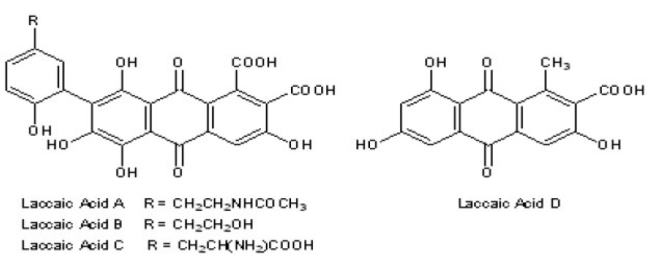
The textiles dyed with these natural dyes are very useful in developing clothing for infants, elderly and infirm people to protect them against common infections. They were equally useful in bed linen, carpets and other home textiles, which are major propagators of common infections.

Review

The extract of *Acacia catechu* (Figure 4.) or *Mimosa catechu* heartwood is brown coloured material used for textile dyeing. The main constituents of the extract dye catechin and catechu tannic acid along with small proportion of brown coloring matter. It also contains tannin, flavotannin, gallotannin, phloratannin etc. as shown in (Scheme 1)[20].

Another source of natural plant dye is *Quercus infectoria* (Gallunt) (Figure 5.) which contains a mixture of (60-70%) gallotannin, ellagic acid 1, starch and glucose. The dyestuff in the tannin of gallnut is ellagic acid and exhibits good dyeing properties because of its auxochrome group (OH) together with other chromogen groups.

Figure 4 : ***Acacia catechu***



Scheme 1 : Chemical structure of laccaic acid

Also, *Rubia cordifolia* (Figure 6) roots contain an organic compound called Alizarin, that gives its red colour to a textile dye known as Rose madder. It was also used as a colourant, especially for paint, that is referred to as Madder Lake. Madder has traditionally been an important natural source of red colour for textiles. However, only three components present in appreciable quantities could be collected chromatographically in large amounts. Purpurin (1,2,4-trihydroxyanthraquinone) 2 is the most abundant colorant (65–67%), followed by munjistin (1,3-dihydroxy-2-carboxyanthraquinone, 10–12%) 3 and nordamncanthal (1,3-dihydroxy-2-formylanthraquinone, 9– 10%) 4.

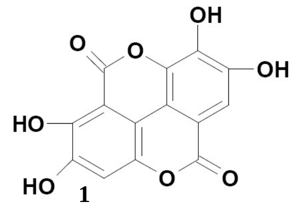


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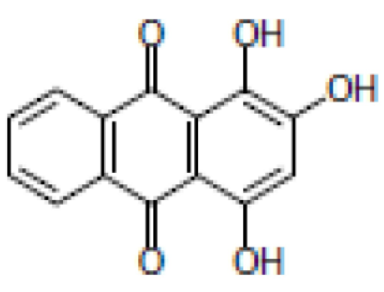
Figure 5 : ***Quercus infectoria***

Another source of natural dye is obtained as a byproduct of the secretion of insect *Kerria Lacca*. It is a species of scale insect of the family Kerriidae (Figure 7). The main colouring component is laccaic acid (Scheme 1), mainly in the form of ammonium salts, which used for dyeing wool and silk fabrics. These pigments are present at up to 10% in stick lac, which has been

Figure 6 : ***Rubia cordifolia***



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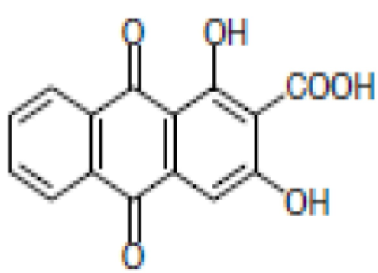

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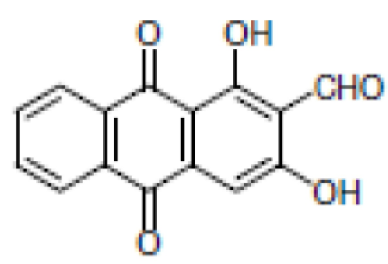

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harvested before adult insects depart their cocoon. Processed seedlac and shellac have a low content of laccaic acids but retain a yellow water-insoluble pigment, erythrolaccin[23].

Figure 7 : Kerria Lacca

Antimicrobial activity of natural dyes on cotton

Balakumar et *al.*, studied the antimicrobial functionality of cotton fabric dyed using natural aqueous dyeing solution obtained by extraction from pomegranate (*punica granatum*). *S. aureus* as Gram (+ve) bacteria and *E. coli* as Gram (-ve) bacteria were used as test organisms for the antibacterial study[24]. This study demonstrated that utilizing the extracted dye significantly facilitate obtaining quality cotton fabrics having both dyeability and antibacterial properties.

Antimicrobial activity of natural dyes on wool

Most of the studies conducted earlier have reported the activity of plant materials against *Candida rugosa*, *S. aureus* and other drug resistant bacteria[25] to check the antimicrobial activity of these compounds when applied on textile materials.

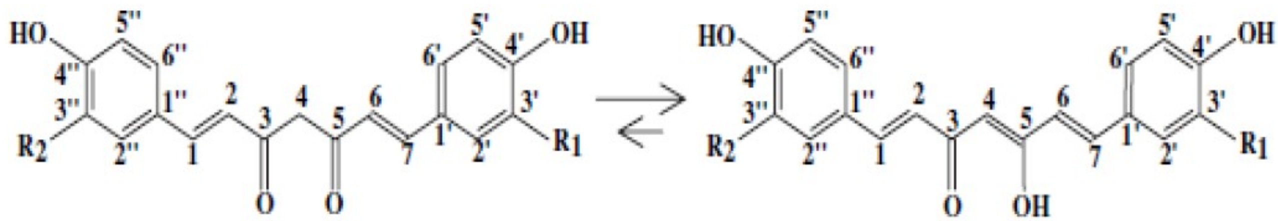
Some researchers have undertaken an interesting study to determine the bactericidal properties of five commercially available dye powders, namely *Acacia catechu*, *Kerria lacca*, *Quercus infectoria*, *Rubia cordifolia* and *Rumex maritimus*, against some common microbes. These dyes tested against common pathogens *E. coli*, *B. subtilis*, *K. pneumoniae*, *P. vulgaris* and *P. aeruginosa*. *Quercus infectoria* dye was most effective and showed maximum zone of inhibition, indicating best antimicrobial activity against all the microbes tested. Minimum inhibitory concentration (MIC) was found to be varying from 5 to 40 mg. The textile material impregnated with these natural dyes, however, showed less antimicrobial activity, as uptake of these dyes in textile material is below MIC. Wool sample dyed with *Acacia catechu* showed a reduction of 10-15% in bacterial growth and a reduction of 15-25% with *Quercus infectoria*. An interesting observation is that the *Quercus infectoria*, exhibited high bactericidal activity in solution and found to be bacteriostatic when dyed onto wool fibre[16].

Moreover, the antimicrobial activity of some other natural dyes (obtained from *Rubia tinctorum*, *Allium cepa*, *Punica granatum L* and Mentha sp.) have been studied against *S. aureus S. sonnei*, *E. coli*, *B. megaterium*, *B. subtilis*, *B. cereus*, *P. aeruginosa*, *S. epidermidis*, *Salmonella* and *P. aeruginosa*. *Puncia granatum* dye was most effective against the test bacteria except *E. coli* and *S. epidermidis*. The textile material impregnated with four natural dyes and maximum inhibition rates (80, 86, 52%, respectively) were obtained against *B. subtilis* of wool samples dyed with *Puncia granatum*, *Allium cepa* and *Rubia tinctorum* while maximum inhibition rates (91%) was found against *P. aeruginosa* of wool sample dyed with *R. tinctorum*[26].

The relation of curcumin concentration and its antimicrobial activity on wool has been investigated[21]. Curcumin has a unique conjugated structure including two methoxylatedphenols and the enol form of b-diketone. It exists in a ketoeenol tautomerism with equilibrium strongly favouring the enol form (Scheme 2). The enol structure enables curcumin to form additional inter- and intramolecular hydrogen bonds. The existence of methoxyl and hydroxyl groups is believed to be responsible for the antimicrobial activity.

Antimicrobial activity of natural dyes on silk

A research study carried out to optimize dyeing conditions of unripe Citrus (Figure 8.). It contains a wide range of flavonoid constituents including hesperidin, naringin, nobiletin and tangerine which are known to show biological activity[27]. Lee *et al. has* optimized the dyeing conditions of unripe Citrus Unshiu extract on silk fabric and evaluate its potential antimicrobial activity on the dyed fabric[28]. The antimicrobial activity of the dyed fabric against *S. aureus* and *K. pneumoniae* has investigated quantitatively. Excellent antimicrobial activity > 99 % reduction rate against two both bacteria was exhibited for all of dyed fabrics.



$R_1=R_2=OMe$: curcumin; $R_1=OMe$, $R_2=H$: demethoxycurcumin; $R_1=R_2=H$: bisdemethoxycurcumin

Scheme 2 : Enol and keto form of methoxylatedphenols (Curcumin)

Synthetic dyes

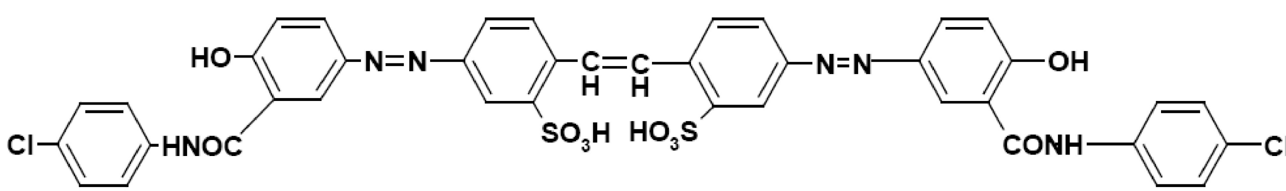
Most of the synthetic azo dyes are widely used in the textile industry[75,76]. The antimicrobial finishing with textile coloration using synthetic dyes are also of great interest. This is due to the fact that textile materials undergo biological degradation, and it seems that about 40 % of the damage is due to the effect of microorganisms. The activity of fungi and bacteria results in the reduced mechanical strength of a material, color change, stains and stale odor. In this regard, the use of dyes with antimicrobial properties extends the service life of these materials, and avoids damage caused by biological degradation. Interestingly, dyes are among the compounds which are suitable for biocidal treatment of textile materials due to the fact that some of them exhibit biological activity, resulting from the presence in their molecule 5of some antiseptic groups that form a definite type of bonding with the molecules of the fibrous material.

Direct dyes

Simu *et al.*, focused on the possibility of developing new eco friendly azo direct dyes 5, 6 with good colouristic and application properties, and exhibiting biological activity[29].

The individual human skin tolerance for these azo compounds evaluated by in vivo imagistic skin studies and the obtained results indicate that, from dermatologic point of view, the azo compounds may be used as textile dyes. Further, the compounds were evaluated for antibacterial activity against *S. aureus*, *S. pyogenes*, *E. coli*, *P. aeruginosa* and *P. vulgaris* by the disk diffusion method. The screening data revealed that the studied azo compounds exhibited antimicrobial activity against most of the tested species, presenting a particular interest against *S. aureus* and *E. coli*.

Acrylic fabric was treated with direct dyes in combination with copper and zinc sulfates as mordanting agents and then tested for their antimicrobial activity against Gram-positive and Gram-negative bacteria. The metal salts used were also studied for their likely effects on the antimicrobial property of fabrics dyed with C.I. Direct Yellow 12, C.I. Direct Red 23, C.I. Direct Red 31, and C.I. Direct Black 38. Untreated (control) acrylic fabric exhibited no antibacterial behavior whilst dyed and mordanted fabrics revealed considerable antimicrobial properties. It was found that the fabric treated with C.I. Direct Yellow 12 and copper sulfate as mordant achieved the highest antimicrobial activity with good washing fastness[30].



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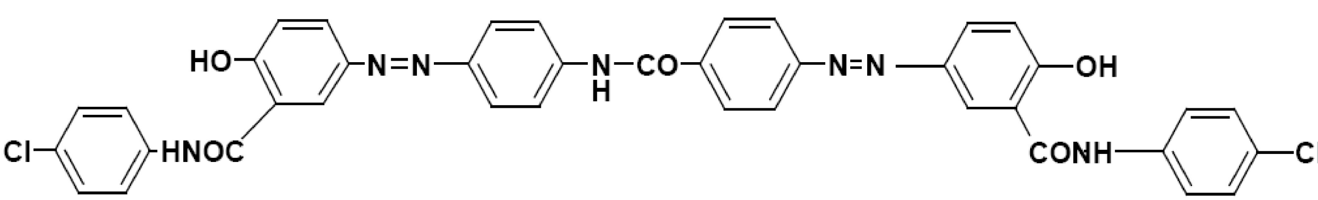

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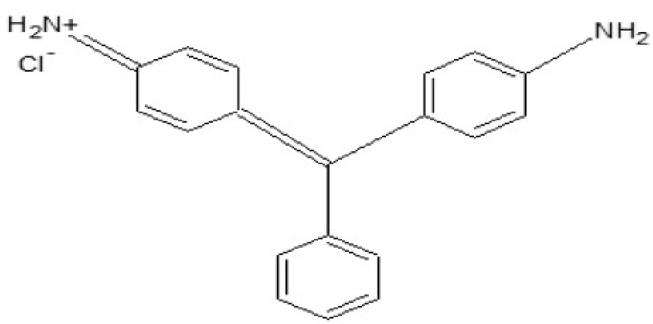
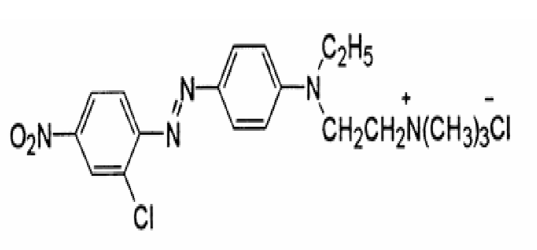
Cationic dyes

Cationic dyes act as bases and when made soluble in water, they form a colored cationic salt, which connect with the anionic sites on the surface of the substrate. These dyes are used in the coloration of acrylic fiber that widely used synthetic fabrics due to a combination of desirable properties, such as soft wool-like handle, good elasticity and mechanical properties[31]

Many cationic dyes possess antimicrobial activity and the most commonly used antimicrobial colorants are triphenylmethane dyes such as Malachite Green (MG, C.I Basic Green 4) 7[32,34]. These dyes exhibited antimicrobial efficiencies because of the presence of quaternary ammonium salts in their molecular structures. Positive electrical charges allow dye molecules to adsorb readily onto microbial surfaces, and then penetrate the cell membrane, followed by destruction of cell membranes and leakage of cell inclusion body. Simultaneously, bacterial enzyme systems are destroyed, causing bacteria death. The cell wall of Gram (-ve) e.g. *E. coli* was more intricate than the cell wall of Gram (+ve) e.g. *S. aureus*, thus such type of dyes adsorb readily onto the surfaces of the *S. aureus* and showed better efficiency against the S. aureus than *E. coli*. The data also showed that antimicrobial effect increases as alkyl chain length increases. However, it was found that alkyl chain length did not significantly affect λ_{max} among these dyes. Dye absorption decreased as alkyl chain length increased, alkyl chains of differing length placed in the dye structure provided antimicrobial efficacy against *S. aureus* and *E. coli*[34].



C.I Basic Green 4 (7)



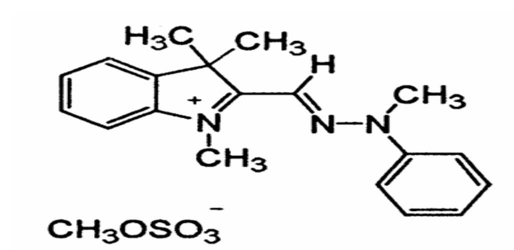
C.I. Basic Red 18:1 (8)

1 Azo cationic dyes

The antimicrobial activity of dyed acrylic fabrics with C.I. Basic Red 18:1 (8) and C.I. Basic Yellow 51 (9) has been investigated against the common pathogens *Escherichia coli, Staphylococcus aureus* and *Pseudomonas aeruginosa*. C.I. Basic Red 18:1 dye was most effective against the test bacteria *E. coli, S. aureus* and *P. aeruginosa* in vitro, whereas C.I. Basic Yellow 51 had a lesser effect. The acrylic fabrics dyed with these dyes, however, showed less antimicrobial activity depending on the dyeing depth[35].

Nine (three series 10, 11, 12) antimicrobial cationic monoazo dyes have been prepared by a diazotization coupling reaction involving two aromatic amino compounds (featuring different chain length alkyl quaternary ammonium salts) as diazo components, and N,N-dimethyl-benzeneamine and 1-phenyl-3-methyl-5-pyrazolone as coupling components. It was found that alkyl chain length did not significantly affect λ_{max} among the nine dyes.

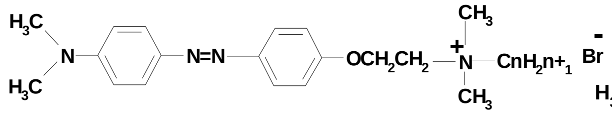
Within dye series 11 and 12, absorption decreased as alkyl chain length increased, but dye series 10 showed the opposite trend. Alkyl chains of differing length placed in the dye structure provided antimicrobial efficacy against *S. aureus* and *E. coli*. The nine dyes had higher antimicrobial efficacy against *S. aureus* than against *E. coli* and longer hydrocarbon chains had better antimicrobial effect with all other factors held constant[37]. The antimicrobial efficacy in aqueous solution of the dye series decreased in the following order: 10 > 11 > 12.



C.I. Basic Yellow 51 (9)

2 Anthraquinone cationic dyes

Some cationic dyes were synthesized in good yield by incorporating quaternary ammonium salt moieties into aminoanthraquinioid dyes. It was found that the di-sub-



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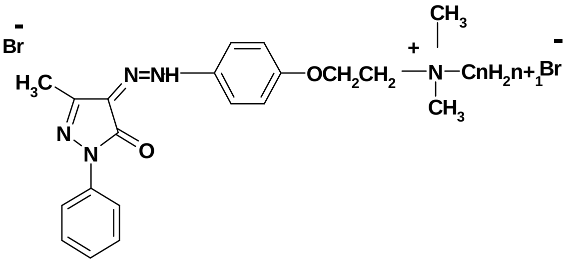
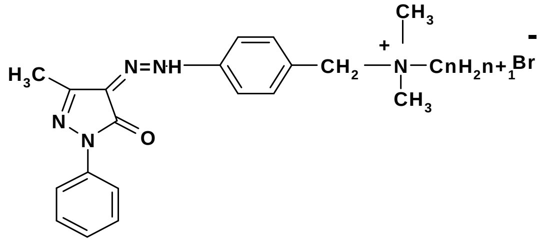




10: 10a (n=3) 10b(n=8) 10c(n=12)
11: 11a (n=3) 11b(n=8) 11c(n=12)
12: 12a (n=3) 12b(n=8) 12c(n=12)
12

11

stituted dyes 13 were of greater bathochromicity than mono-substituted dyes 14. An increase in the alkyl chain length in QAS lowered the λ_{max} of the dyes. All dyes exhibited antimicrobial efficacy against *S. aureus* and *E. coli*, with di-substituted dyes usually showing higher activity. It was also found that the alkyl chain length in QAS played an important role in antimicrobial functions. Lower than eight carbons in the QAS alkyl chain led to very low antimicrobial activities. In addition, the antimicrobial dyes provided higher antibacterial efficacy against Gram-negative bacteria than Gram positive bacteria, which could be due to the structural differences between bacteria[36,38,39].

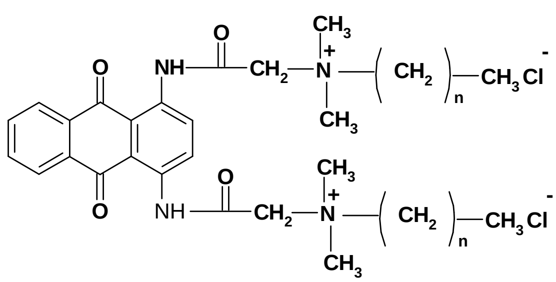
3 Cationic-reactive dyes

Different approaches have been made to unify dyeing and functional finishing in one bath by preparing dyes that have color and additional functional properties together. For example, antimicrobial cationic dyes were prepared by incorporating long alkyl chain quaternary ammonium salts (QAS) to anthraquinone chromophores through covalent bonds[40]. These dyes showed excellent color and antimicrobial functions in solutions and could be effectively introduced to acrylic fibers to achieve simultaneous coloration and antimicrobial efficacy. However, these dyes do not have affinity to cellulose. The synthesis and characterization of the cationic reactive dye based on monochlorotriazine reactive group as well as its applications in dyeing cotton fabrics have been discussed[41]. From which, a quaternary ammonium salt dye structure with the long chain length of 12 carbons was chosen since longer alkyl chains, shown in (Scheme 3), are more effective as antimicrobial agents. Meanwhile, the anthraquinone chromophore renders good chemical stability. The dye demonstrated adequate antimicrobial properties in aqueous solution.

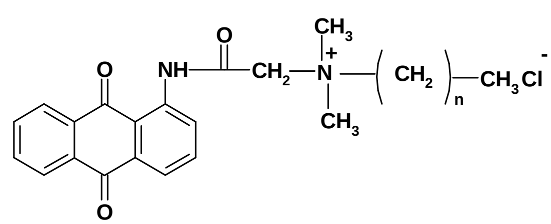
It was found that the dye exhibited adequate antimicrobial activities against both Gram positive and Gram-negative bacteria at a concentration of 10 ppm. The hydrophobic characteristics may increase the antimicrobial function of the cationic reactive dye. This cationic dye also can react with cellulose to dye cotton without using any electrolyte as dyeing assistant. The dye exhaustion and fixation rates on cotton were reasonably high without significant hydrolysis, and the dyed cotton exhibited good color washfastness. However, the washfastness of the antimicrobial functions of dyed fabrics was unreasonably low.

Reactive dyes

Concerning the direction of synthesis of reactive dyes based on quinazolinone moiety[42-44], Divyesh and Keshav reported a facile and convenient synthesis of



n=3, 7, 11 **13**



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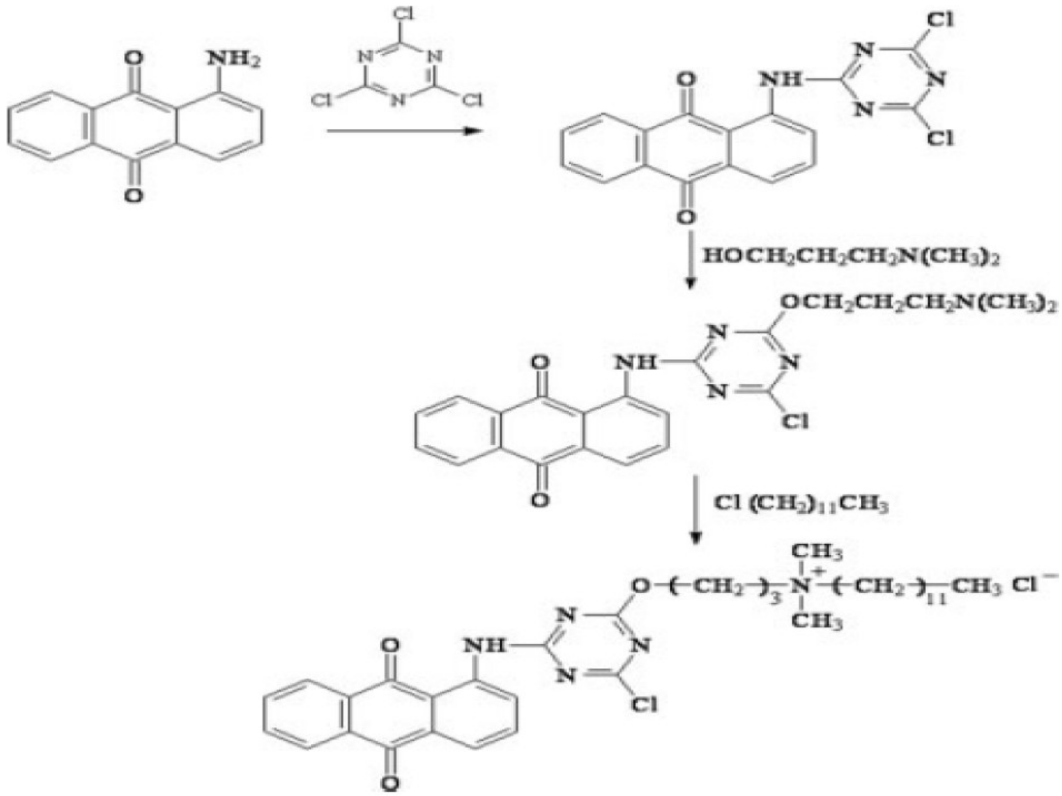


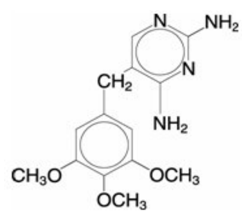
Scheme 3 : Synthetic procedure of antimicrobial cationic reactive dye

novel quinazolinone reactive dyes and studied their dyeing properties, fastness properties, antimicrobial activity, colorimetric data and solvent effect[45]. The synthesized novel reactive dyes not only give good dyeing property but also showed pharmacological activity *i.e.* antimicrobial activity. In this regard ten monoazo quinazolinone based reactive dyes (16 a-j) were made by coupling of diazotized 3-{4-[4-amino-2-nitrobenzyl]-3-nitrophenyl}-7-chloro-2 phenylquina-zolin-4(3H) one with various p-chloro anilino cyanurated coupling components (15a-j) as mentioned in (Scheme 4)[45].

Trimethoprim 17 and sulfamethoxazole 18 have been modified to act as reactive dyes for cotton to impart antibacterial properties. Some of the treated fabric was subjected to multiple washings to determine durability. The treated fabrics were then assayed for antibacterial properties. The results indicated that these compounds may be used to attach specific antibacterial compounds to cotton fabric to create specific usage, designer, or tailored fabrics to meet specialized needs[46].

Disperse dyes

Disperse dyes are organic colours having less water solubility, these are applied in colloidal aqueous dispersions to hydrophobic textile fibres in which the dyes



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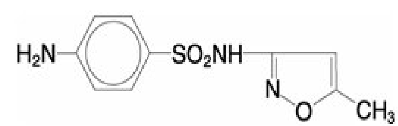

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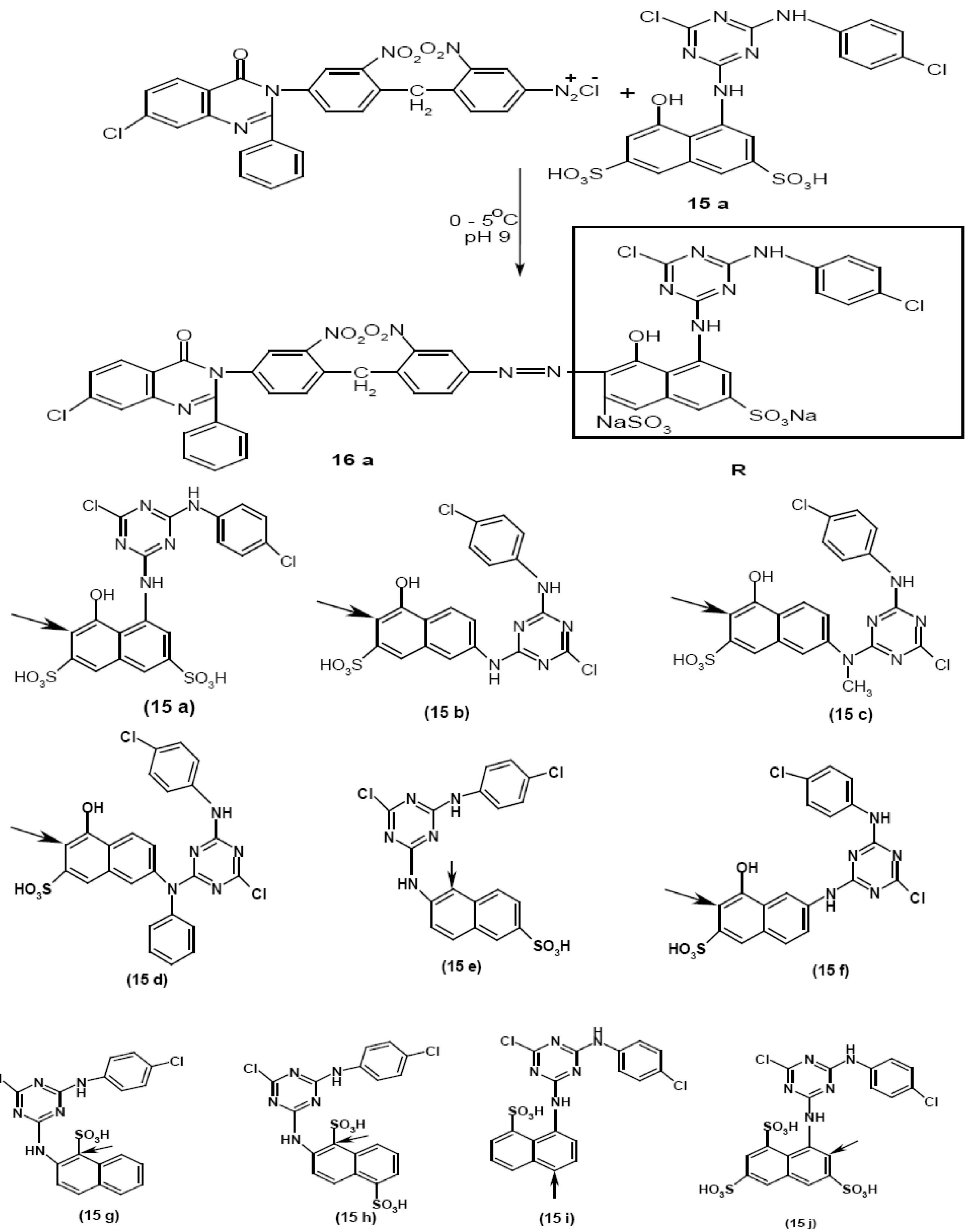
literally dissolve and produce desired coloration. The development of disperse dyes is due to significant increase in the world production of polyester fibres as compared to other fibres. Over 90% of disperse dyes usage is for the coloration of polyester and its blends. A monoazo dye with a heterocyclic system is very useful class of disperse dyes[47-49].

Thiazole based disperse dyes

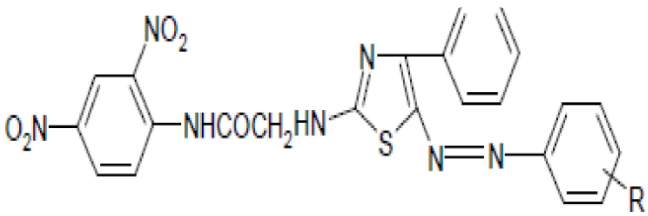
Various diazotized aryl amines were coupled with N-(2,4-dinitrophenyl)-2-[(4-phenyl-1,3 thiazol-2-yl) amino]acetamide to give the corresponding various azo disperse dye structures 19. These dyes were applied to polyester fabric and their fastness properties were evaluated. These dyes showed very good anti-microbial activities. The wash-fastness of all the compounds, as may be anticipated on the basis of their increased molecular weight and polarity to less substituted analogues, was also of an acceptably very good order. In-



Scheme 4 : Monazo quinazolinone reactive dyes, R= various ρ-cloroanilino cyanurated coupling component (15a-j)

troducing the terminal amino group for better dispersibility observes no notable change in the percentage exhaustion. Overall, the prepared dyes gave generally good dyeing on polyester fibres. All the samples showed moderate activities against *E.coli* and *P. aeruginosa*. These dyes showed good antibacterial activity against above bacteria and destroy the progressive cell of microorganisms[50]. The synthesized dyes were screened for their antimicrobial activity[51-53] using disk diffusion method using different bacterial strains such as Gram (-ve) e.g. *E. coli, P. aeruginosa*, Gram (+ve) e.g. *S. aureus* and fungi C. Albicans with 40µg/ml concentration.

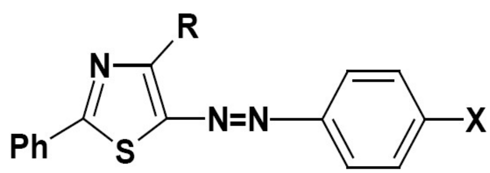
A dibenzobarrelene derivative 20 have been used as key intermediates for the synthesis of 5-(arylazo) thiazole disperse dyes. The synthesized dyes were applied to polyester and their antibacterial, color measurement, and fastness properties have been evaluated[54].



19; R= H,-OH,-CH$_3$,-NO$_2$, -Cl, -Br

Pyridine based disperse dyes

Pyridine derivatives are relatively recent heterocyclic intermediates for the preparation of dyes (Scheme 5). The azopyridinone dyes give bright hues and are therefore of investigative interest. Owing to their improved brightness and light fastness, pyridinone disperse



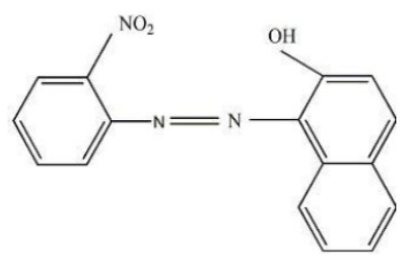
20; R= CH$_3$ or Ph and X = H, CH$_3$, OCH$_3$, CL, Br, NO$_2$ or COOEt

dye derivatives have found many applications on different fibres[55]. Moreover, the pyridinone nucleus has been proven to constitute the active part of several biologically active compounds[56]. The synthesis of 4-methyl-2,6-dioxo-1-propyl-1,2,5,6-tetrahydro-pyridine-3-carbonitrile 23 as a good precursor to novel aryl- and heteroaryl -4-methyl- 2,6-dioxo- 1-propyl-1,2,5,6-tetrahydropyridine -3-carbonitriles and their application as disperse dyes for the dyeing of polyester fabrics. The antimicrobial activities of the synthesized dyes were screened against selected bacteria by the disk diffusion method and their inhibition zones diameters reveal that three of the tested dyes showed positive antimicrobial activities against at least one of the tested microorganisms. Two dyes, 22a and 23a showed strong activities, while two dyes 23b and 23c showed moderate activities with significant inhibition zones >10 mm, against Gram (-ve) e.g. *S. auerus* and *B. subtilus*. It is worth mention here that dye 22b has showed no antimicrobial activities against any of the tested microorganisms, and all the dyes have no antimicrobial activities against Gram (-ve) e.g. *E. coli, K. pneumoniae* and *P. aeruginosa* due to bacterial structure[57].

Naphthol based disperse dyes

In the field of azo dyes, phenolic compounds play a major role for synthesizing most of the commercial dyes[58,59]. The synthesis and characterization of 4-methoxybenzeneazo-2'-naphthol and 2-nitrobenzeneazo-2'-naphthol dyes and their application on wool, silk and nylon fabrics have been investigated[60]. The results showed better hue with good colorfastness to washing, rubbing, and light. The dyes were also evaluated for *in vitro* antibacterial activity against different strains of gram-negative and gram-positive bacteria. The results of the antibacterial properties of these dyes revealed that both the dyes were resistant to aerobic bacterial degradation but dye 24 showed more antibacterial effect than dye 25.

The results showed that both the dyes exhibited very slow rate of oxidation and inhibited bacterial growth. This can be attributed to the fact that enriched electron cloud of naphtha moiety arising from electron donating power of O$^-$ centre could actually be drifted to nearby vacant π* orbital of azo (N=N) group[61]. Amongst these dyes, the rate of oxidation of dye 26



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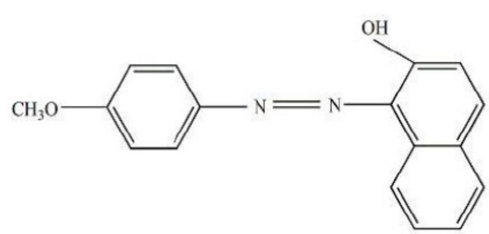

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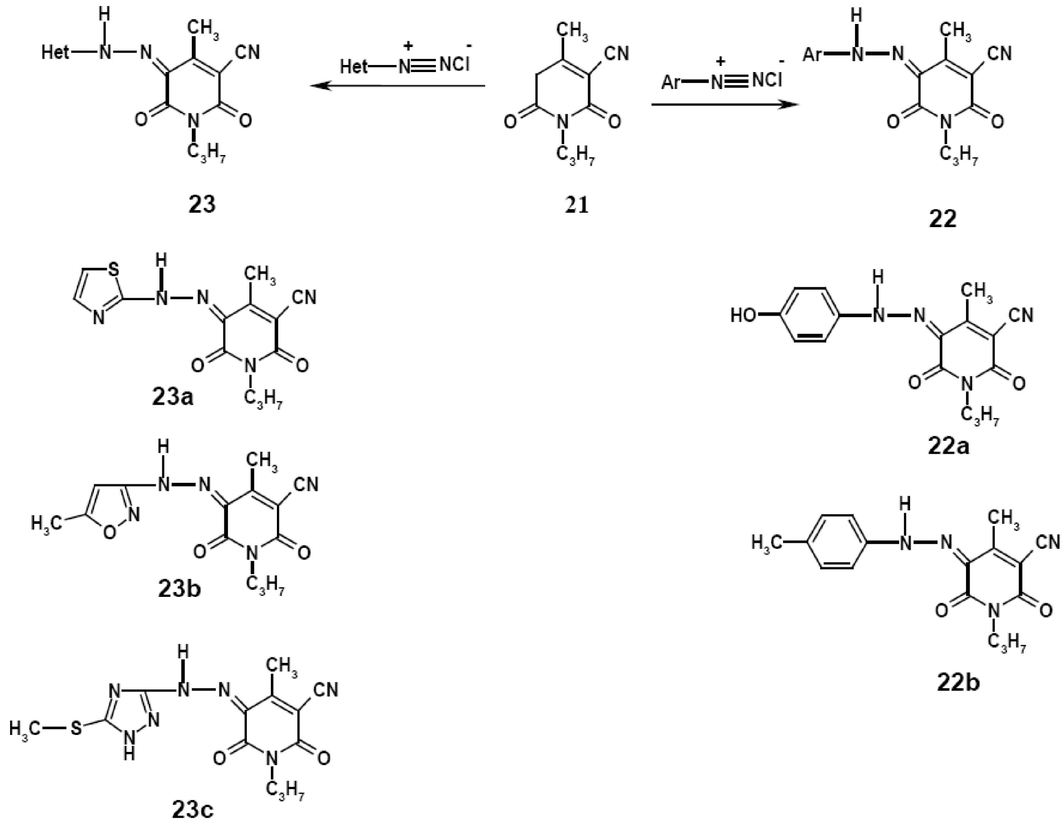

Scheme 5 : Diazotization reaction of Pyridinone derivatives

was comparatively lower than that of dye 27 as the former dye possesses a strong electron withdrawing group $-NO_2$, the electron density in the diazotized benzene nucleus is further reduced and consequently the rate of oxidation of the dye was subsequently reduced. This might also be the cause of its more antibacterial effect.

CONCLUSION AND FUTURE PERSPECTIVES

The exponential increase on the development/performance of antimicrobial dyes provides a measure of their great potential and the significance of bolstering the research regarding improvement of their synthesis, as well as their activity and the mechanisms of action. It is crucial to achieve innocuous materials, non-cytotoxic, to the human beings with potent and broad range of antimicrobial activity, long-last response and even reusable to maintain the activity, always keeping in mind the environmental and recycling aspects.

As shown through this review, there are many strategies to design synthetic antimicrobial dyes based on azo heterocyclic and/or homocyclic Systems including natural dyes with diverse manners of action over microorganisms. Their activity may be inherent in their original structure, because of chemical modification to confer the resultant biocidal behavior. Most research has been focused on polycationic systems that are more straightforward and synthetically flexible. Therefore, progress will be concentrated on the increment of their selectivity and durability. However, dye systems based on the antimicrobial agent are in the lead commercially. In this sense, their improvement will come by incorporating the antimicrobial agent such that toxicity will be reduced while activity is maintained or enhanced, i.e., encapsulation. In addition, special effort will be done in the area of nanotechnology, in which a small amount of active component, less than 5 wt%, renders the whole system effective. Cytotoxicity reduction will be another goal, which is not a problem in areas of decontamination or antifouling where they will have a great potential. Efforts will be also focused to reduce cost by investigating inexpensive dye systems. In short, the future of these materials will go through a combination of the different approaches, continuous investigation on the killing action of these promising systems.

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