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Original Research Article

Synthesis, Characterization and Applications of Mono Azo, *o-o* Metal Complex Dyes of Cr(III), Fe(II), Co(II) and Cu(II)

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Abstract

Diazo compounds of 2-aminobenzoic acid with H-acid and 4-Napsa as coupler and their metal complexes were synthesized and characterized by various spectroscopic techniques like UV, FT-IR, NMR and colorimetric studies. The color data analysis showed their active participation towards the fastness properties on fabric twils. The resultant dyes were then screened against gram negative, positive bacterial and fungal strains which gave promising results.

Keywords: Dyes, spectroscopic studies, colorimetric studies, microbial strains, Twills.

INTRODUCTION

Colored substances which have the tendency to react and can be applied to the substrate molecule are called dyes. In order to increase the citadel property of the dye they need a mordant and are usually applied in the aqueous solutions.

In most of the cases both (dyes and pigments) seem to be colored due to ability of absorbing some light wavelengths than others. When we compared the dye with pigment, pigment is generally is insoluble in aqueous solution and has no combining ability (affinity) towards the substrate [1].

Dyes are actually complex organic compounds which are widely used in color textile, fur, hair, leather, drugs, petroleum products, cosmetics, waxes, paper greases and plastic. “They remain persistent in these substances through salt /metal complex development, biophysical adsorption or through the covalent bonds formation [2].

1.1.1 Characteristics of dyes

(i) Colored substances which have the tendency to react and can be applied to the substrate molecule are called dyes.
(ii) To increase the citadel property of the dye they need a mordant and are usually applied in the aqueous solutions.
(iii) Dyes provide an enormous degree of coloration when react to matrix.
(iv) Dyes must have fixation ability [3].

1.1.2 Brightness

Absorbance bands shape always described the brightness very nicely. If band is narrow then dye would have been very fast. When it is broad the dye would be dull. It is prominent from the above statement that brightness of the substance always depends upon the amount of reflection of light [4].

1.1.3 Light fastness

The fastness of light of a fiber being dyed generally enhances with raising the concentration of dye. The main reason is elevation in average size of submicroscopic particles of dye which it forms with fiber. A Light fastness of textile dyes are directly linked with physical characteristics and chemical structure of the fiber. The citadel property is effected due to the concentration, mordant type and nature of fiber [5].

1.1.4 Fiber properties

The fibers of mature cotton forms a flat ribbon having difference in their width ranging between 12 and 20 µm. It is extremely difficult due to account of the distortion that takes position at the time of formation of tubular shape in growth collapses when subjected to drying. The convolutions numbers vary (four and six

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per millimeter) causing reverses the direction after every millimeter along the whole fiber. These key factors make the fiber easy to identify under optical and electron microscopes [6].

1.2 Sources of dyes

There are two main sources of dyes

1.2.1 Natural Sources

In this source, dyes are achieved from natural ways (animals and plants). These are being used for coloring natural fiber such as (wool, cotton, silk, fur and leather). Natural dyes are also being used for the production of inks, cosmetics and paint emulsions.

1.2.2 Synthetic Sources

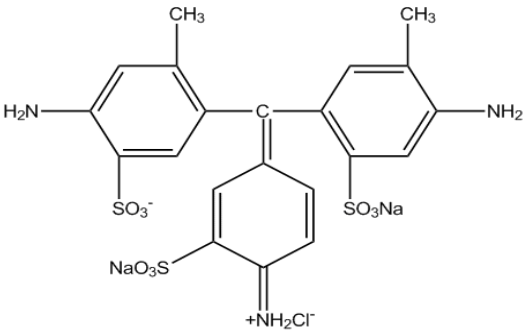
Synthetic dyes change the natural dyes and produce colors that were unreachable prior to artificial dyestuff. When the synthetic dyes smack the natural dyes in clarity and consistency. Synthetically indigo, tyrant purple, alizarin, and several additional dyes were formed with very little price from substance from coal tar. They have less cost, imparted better properties to the dyed materials and offered a vast range of new colors, [7]. Owing to extensive ranges these dyes are classified into subsequent categories [8].

1.3 Classification of dyes

Classification of dyes on the basis of application.

1.3.1 Acid dyes

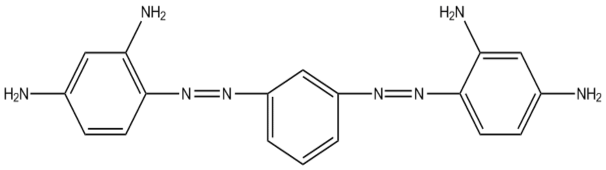
Such dyes are applied usually on an organic or an inorganic acid. These can be simply applied on wool, protein and polyamide fibers. These dyes create a broad range of glowing shades like acid Magenta is not very rapid to milling whereas Orange Red is very rapid. The dyes belongs to this class were ended by Nicholson in 1862 [9].



Acid Megenta

1.3.2 Basic dyes

Basic dyes are usually ionized in to colored cations and colorless anions. The colored section is derived from free or substituted amino groups functionalities such as dimethyl amine, diethyl amine and ammines. For example Bismarck Brown which is generally insoluble in water and to pass on solubility. These bases are renewed in to their hydrochlorides, oxalates, acetates, sulphates, nitrates or zinc chloride double salts [9].

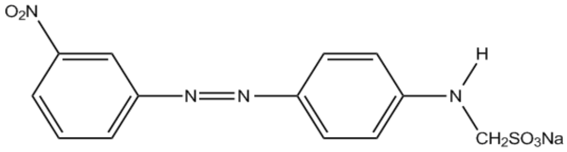


Bismark Brown

1.3.3 Disperse dyes

The disperse dyes are organic coloring substance which remains free from ionizing groups, having low water solubility and suitable for dyeing hydrophobic fibers of colloidal dispersion. Dyes of natural fibers (cotton, wool and silk) which is effectively hydrophilic in nature and entails the usage of water soluble and temporarily solubilized the stuffs of dyes. Dyeing is more or less forever based upon aqueous system. When hydrophobic fibers made their appearance, they offered an extremely severe dilemma. So, they cannot be dyed with the dyes available. As a result of this, when cellulose acetate was begins, its dyeing behavior occupied broad awareness. Attempts were made in this field, which has resulted in the development of acetate dyes (Ionamine Yellow MA) [9].

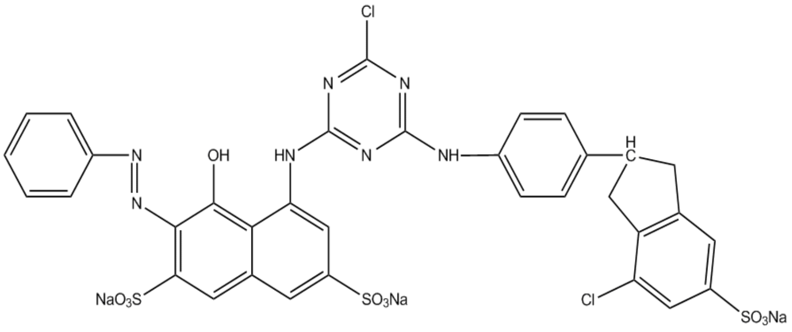
Acetate and their related dyes were later on opens to be suitable for dyeing and printing and much other man made materials from polyamide and polyester fibers. After huge experimental and practical work produced these compounds which were hydrolyzed in water preferably and liberating the highly soluble base of quite simple structure to be immersed through the acetate fiber [9].



Ionamine Yellow MA

1.3.3 Reactive dyes

Reactive dyes can react with the substrate and forms covalent linkage or co-ordinate covalent bonding. Bond formation of dye fiber is increased by alkali and it is very rapid and irreversible. These dyes are characterized through high solubility in water, low cellulose affinity, compatibility and highly suitable for continuous application to viscose rayon and cotton linen by padding technique. They may be used to polyamide fibers to produce bright dyeing as acid wool dyes. They have similar wet speed to dyeing of vat dyes and are of huge interest for printing cellulosic materials. Since brightest colors with extreme fastness to wet and light treatments can be formed through direct printing using sodium alginate thickening, sodium bicarbonate and containing urea like Direct Brilliant Pink G [9].

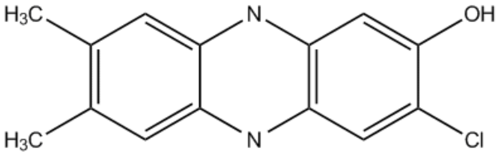


Direct Brilliant Pink G

1.3.5 Sulfur dyes

Sulfur dyes are the heterocyclic organic compounds. They are prepared when nitrogenous compounds react with Na_2SO_3, Sulfur or sulfurizing agents. Sulfur dyes are commonly applied dyes prepared for cotton. Sulfur dyes are easily used and have good washing fastness. From the dye bath they are incorporated in cotton in the presence of Na_2SO_3 or sodium hydro-sulphite and made insoluble inside the fiber through oxidation. During the course of development these dyes provide a larger molecule complex which is base of high quality wash fastness.

Sulfur dyes are commercially used in many countries throughout the world for several decades. Durability and flexibility are two characteristics of sulfur dyes. Black, Blue and Brown dyes are highly significant for point tonnage [9]



Eclipse Brown 8R

Sulfur dyes are very important for creating the broad range of shades on fabrics like rayon and cotton, especially upon the heavy durable shades (apparel fabric). These dyes are comparatively cheap among all the synthetic dyes. Their light and washing fastness are usually outstanding but have variations from dye to dye. Their shades and fastness towards powerful oxidizing agents (sodium hypochlorite solution) is very dull and poor. Sulfur dyes are not absolute in terms of shade range. Because true Red is not present in the class [9].

The oxidation can be completed in air or by using oxidizing agents like hydrogen peroxide or sodium bromate in a mildly acidic solution. These are very important for dyers work. The traditional black color is obtained from sulfur dyes ranging up to 50%.

1.3.6 Azo dyes

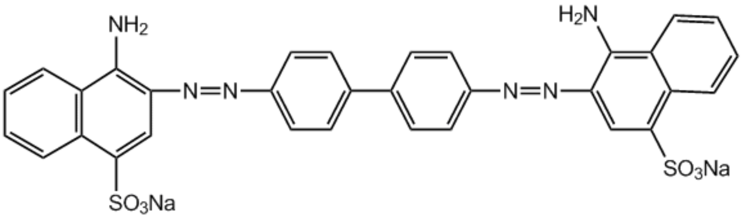
Group of dyes which are characterized by double bonds of nitrogen to nitrogen are called azo dyes. They are the highly usable dyes in the textile industry account the over 50% of all commercially used dyes. Still huge quantity of azo dyes stay in the sewage water following the completion of dyeing processes and the majority of azo dyes are non-biodegradable [10]. Therefore, successive biological treatments are approximately non effective on the textile effluents color. So, the textile waste waters are profoundly colored with huge differences in their chemical composition.

1.3.7 Metal complexed azo dyes

Azo compounds are extremely colored and are used as pigments and dyes for a long time. They have been widely used in several useful applications like coloring fibers, printing systems, photo electronic applications, textile dyes, optical storage technology, various other biological reactions as well as in analytical chemistry [11].

1.3.8 Direct Dyes

These dyes are directly attached with fabric through its substantive control like hydrogen bonding or without any type of chemical bonding are termed as direct dyes. These dyes are mostly used in cotton dyeing industry. Direct dyes are commonly applied on the cellulose fibers (cotton, viscose, rayon). Commonly these dyes are easily dyed from the simple solutions in water, and cold water in some cases. So, these are also known as direct cotton dyes. These dyes are held together through Van der Wall/electrostatic forces and hydrogen bonding. Approximately, 75% of direct dyes utilization is for cellulosic fibers dyeing like Congo Red.



Congo Red

1.4 Photochromism of direct dyeing

Some direct dyes (sulphonated copper pthalocyanines) demonstrate the photo chromic alter the cellulosic fibers. The shade altering from sharp bright turquoise to violet or reddish blue when exposed to sun light or ultraviolet radiations. The change in color slowly to the original turquoise on withdrawal of the illuminant. This cause is due to incidence of fixing agents of dyes mostly. In case of dyed material storage, a decreasing effect is produced in descending order. The chromed change is linked with ultraviolet radiation and the moisture content. If the radiation source is not available the reversal to parent color is very easy in the dry scenario. In moisture dependent products the resist in crease vanishes rapidly. The photo chromic activities of copper anthranyl direct dyes become visible to pursue a redox mechanism. On dyeing the cellulusic fibers when they are subjected to the vetting procedure with (NaCl and acetic acid) the color changes occur very fast. "It is very interesting to note that the unsulphonated copper anthranyl dye do not exhibit this redox behavior.

1.5 Application behavior of direct dyes

In the presence of an electrolyte dyes are extensively applied on fiber. Their behavior is dictated by four aspects.

(a) In direct dye solution when fibers are soaked they immerse dye from the solution until equilibrium, so most of the dye is used up by the fibers.
(b) The rate of come out to stability specific for each dye.
(c) At equilibrium is the collapse is linearly associated with substantively ratio. In the dye bath, this is the amount of dye soak up by the fiber to the residual.
(d) The measure of substantivity of the dye for fiber at equilibrium is denoted by exhaustion.

The strike is defined as the uptake of direct dye by the surface of fiber which is a pivotal point in dyeing. The dispersal of the dye into the fiber is the later case allocations of dye come close enough to attain equilibrium. Complete diffusion into the core of the fiber is significant to entirely attain the preferred shade and fastness properties. Key factors upsetting the direct dyes absorption through cellulosic fibers including the temperature and time of dyeing, salt concentration, liquor ratio and behavior of aggregation and solubility of dyes. Penetration and strike rate are increased on elevated temperature and absolutely temperature dependent. The time of dyeing is decreased above the boil temperature ultimately increasing the full penetration of dyes in fiber. The equilibrium collapse is decreased due to amplification in the dyeing temperature which enhances the rate of dye absorption. Optimum temperature conditions are of great deal for permanent dyeing. By increasing the time of dyeing assimilation and penetration is usually favored. The liquor ratio, solubility, leveling properties and strike rate dictate exhaustion. During the process of dyeing substantial difference can be established depending upon the liquor ratio on fibers. The substantivity and strike rate increases due to the accumulation of electrolyte in the dye bath. The amount of electrolyte necessary depends upon the chemical structure and dye concentration in the dye-bath in each molecule, largely the number of sulphonic acid groups. At room temperature very low liquor ratios are obligatory in padding process for excellent solubility. In order to avoid less penetration, rough dye absorption care has to be taken which reveals that alteration occurs in the dyeing action. The time of half dyeing is also an important characteristic of direct dyes which determines that how much fiber has soaked the dye. The choice of mixtures become appreciating due to the consideration that all the dyes have similar time of half dyeing. This analysis was consequently revealed to be fictional when rate of dyeing was inadequate to forecast compatibility, salt control and rate of migration are of equal importance.

The society of dyers and colorists recommended that direct dyes can be classified as follows. Class first, Dyes that are 'self levels', that is dyes of good migration and good leveling properties.

Class second, Dyes that are not self-leveling, but can be controlled by the addition of salt to give level results; these are described as salt 'controllable".

Class third, such dyes are simply called temperature controlled because their exhaustion is absolutely temperature dependent and sensitivity to salts. Comparative mixtures are used for the suitable selection in classification of all the three classes for the study of exhaust dyeing. Different temperatures are very helpful for determining the substantivity at wide temperature range. The exhaustion of dyes is studied at optimum conditions of liquor ratio and concentration of electrolyte. Twil was dyed in the dye bath until the dye concentration become poor in the solvent. The same process was implemented for the remaining samples which should be used later for the colorimeteric studies. Very apparent alteration in color is indicated by the samples [12].

1.6 Dye-bath variables that influence dyeing Behavior

The principal parameters tendering the assimilation of direct dyes through cellulose from aqueous solution are temperature, liquor ratio, time of dyeing, solubility of the each dye, salt controllability and lesser level the manipulation of auxiliary agents.

1.6.1 Temperature

Strike and fiber penetration are direct through application temperature and can be enhanced through temperature increase. Dyeing above the boiling temperature has shorten the period and improving the penetration of dyes. The outcome of increase in temperature is to improve the dyeing rate but to reduce the stability exhaustion. (As a result of this permanent dyeing time there is an optimum temperature at which absorption is at maximum achievable level.

).

1.6.2 Time of dyeing

The production of well penetrated dyeing is generally superior by an improved timing of dyeing but delayed the dyeing at the boil when a number of consecutive addition of dye are prepared for corresponding purposes occasionally consequences in the breakdown of direct dyes.

1.6.3 Liquor ratio

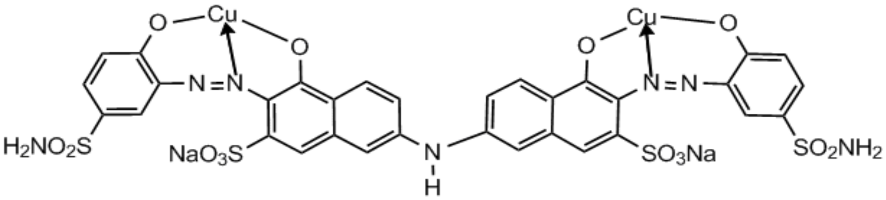
Due to liquor ratio dyebath exhaustion occurs but we have to keep vigilant consideration regarding strike rate, solubility and leveling properties in water. Liquor ratio dictates the sequential changes in dyeing the cellulosic fibers. Padding process can be managed at incredibly small liquor ratios (jig methods operate at 3:1 to 5:1 and loose stock or yarn on wound packages are dyed at about 10:1). Larger liquor ratios are effective when dyeing fabrics in winch about 20:1 to 30:1 overflow machines or jets at 5:1 to 15:1.

1.6.4 Dye solubility

Dyes of fine solubility are perfect for wrap up dyeing and predominantly at the little temperature and liquor ratios essential in padding process. The water supply for pad liquors should have little electrolyte content.

1.6.5 Salt controllability

Salt sensitivity is the level of direct dyes which influenced the addition of electrolyte in the dye bath. Direct dyes alter significantly with the producation of electrolytes. The dye strike rate is amplified through the electrolyte addition. (In general the lower the ratio of relative molecular mass to number of sulphonate groups per molecule, the less incorporation can happen with out electrolyte addition, The electrolytes used as glauber's salt (sodium sulphate) and common salt (sodium chloride), the last being favored with hard water). The role of different electrolytes in promotion of dye bath exhaustion has relation with dye structural features. Cotton can be dyed under neutral conditions with two purified direct dyes turn over in comparative molecular mass and degree of sulphonation, in the occurrence of different electrolytes and phosphate buffer system. It was observed that univalent electrolytes (calcium chloride) were more effective in promoting the dye bath exhaustion. “The outcome of alkali metal ions, quaternary ammonium ions, bivalent and trivalent cations on the absorption of C.I Direct Violet 66 by viscose fibers at various temperatures has been examined.” Dye assimilation does not emerge to depend upon the charge of cations current but merely on their size. A convincingly good linear relationship was established between the saturation values in the survival of different ions and their ionic radii. The rate of absorption also enhanced with an amplification in the size of cation, particularly at very low temperature. The divergence in the rate and degree of absorption relative to ion size tends to decrease when temperature is increased. “Equilibrium adsorption isotherm and rate of dyeing of C.I Direct Blue 1 on viscose fibers at various temperatures were determined in the presence of electrolytes having unsurprisingly different capacities to modify waters structural characteristics”. The results evidently confirmed that variation in water molecular clustering around the “hydrophobic portions of the dye molecules and cellulosic fiber surface control the dye binding mechanism”.(In the presence of single electrolytes the incorporation of C.I Direct Blue 1 by viscose fibers and the rate of dyeing at constant electrolyte concentration increased in the order. In binary mixtures of these electrolytes the cations with the greater ability to disrupt the clusturing of water molecules the ion with larger radius could considerably enhance the tendency of smaller cation to influence dye incorporation and dyeing rate. C.I Direct Red 28 is a highly aggregated dye). When it is applied to viscose fibers in the incidence of electrolytes accomplished of modifying water's structural character in an expected manner the integration and rate of dyeing are extremely close to those for much fewer aggregated ionic dyes. Thus even though this dye demonstrates strong affinity to form huge aggregates by electrostatic hold between cationic ammonium and anionic sulphonate substituent groups. The manipulation of electrolyte cations on the clustering of water molecules nearly clusters and substrate surface remain unaffected.



Direct Violet 66

1.7 Fixation of dye in fiber

Stereochemical studies have shown that hydroxyl groups present in the fiber are responsible for the hydrogen bonding. Cellulose is the polysaccharide of beta D glucose which are linked through one four linkage.

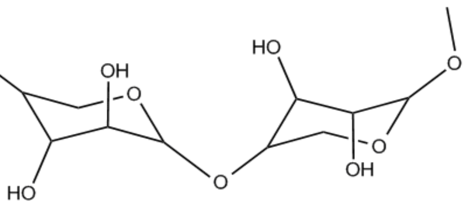


Fig-1.1: Structure of cellulose

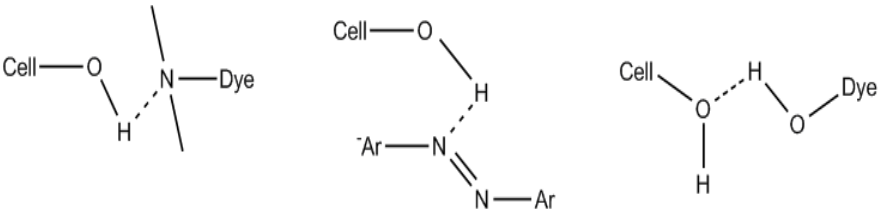


Fig-1.2: Hydrogen bonding between celllose and polar groups

1.8 Some metal complexes of azo dyes

There can be a little doubt that, metal complexed azo compounds are by far the most important. With widely used metal complexed (dyes and pigments) by possible exception of copper phthalocyanine. Metal complexed azo compounds may be divided conveniently into two classes, those in which the azo group does not forms a part of metallizable system, and those in which it does. The later class is more significant and is derived from azo dyestuffs having metallizable substituents having at least one ortho position relative to azo group C_1. Little commercial applications are encountered due to substituents other than those in C_2. Other dyestuffs relative to the azo group for chelation to occur have a heterocyclic nitrogen atom in an appropriate position. Commercially metal complexed azo dyes in which azo group does not form a part of chelating system are far less impotant, and they are obtained from the dyes derived from metallizable coupling components such as salicylic acid (XIX), 8-hydroxyquinoline, salicylaldoxime and salicylaldehyde [13]. The metals most commonly used are copper in the field of cotton dyestuffs similarly chromium and cobalt in the field of wool dyestuffs. Because of the low stability to acid treatments, copper complexes find little application as wool dye stuffs, but with the advent of fiber reactive dyes (chromium/cobalt) dyes are gaining popularity as dye stuffs for cellulosic fibers.

Aims and Objectives

Keeping in view the properties, the thesis is designed with the following aims and objectives.

1. To synthesize the eco-friendly dyes for the replacement of (carcinogenic) dyes.
2. To study the synthesis of (mono azo dyes) along with their (metallization)
3. process parameters.
4. To study the spectroscopic aspects like Uv-visible and FT-IR.
5. To study the (antimicrobial activity) of the (metallized dyes).
6. To study their color citadel properties.
7. To study the constitutional effects.

MATERIALS AND METHODS

2.1 Chemicals used

1. 2-aminobenzoic acid
2. 8-amino-1-naphthol-3,6-disulphonic acid (H-acid)
3. 3-amino-1-hydroxy-5-nitro benzene sulphonic acid (4-napsa)
4. Chromium acetate
5. Ferrous sulphate
6. Cobaltnitrate
7. Copper sulphate
8. Sodium acetate
9. 30% Hydrochloric acid
10. Acetone
11. Ethyl alcohol

12. Dimethyl sulfoxide
13. 2% agar solution
14. Methanol

2.2. Apparatus used

1. Electric motor as stirrer
2. ice bath
3. pH meter
4. beakers 250 $cm^3$and $1dm^3$
5. Thermometer 0°C- 100°C
6. Funnel
7. Pipette
8. Measuring cylinder
9. Drying oven
10. Chromatographic tank and paper
11. Micropipettes
12. Aluminum foil
13. Petridishes

2.3 Synthesis of metal complexes of sodium[8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate].

General procedure

2.3.1 Diazotization

2-amino benzoic acid (0.0025 moles, 0.45g) was dissolved in 15-20 ml HCl (30%) at room temperature. The solution was then cooled to 0-5 ºC in an ice bath and maintained at this temperature, solution of sodium nitrite (0.0025 moles, 0.17g) in water (10-15 ml) was added dropwise within 20 minutes under constant stirring and the mixture was stirred at 0-5ºC for 1 hour.

2.3.2 Coupling

The coupling component 8-amino-1-naphthol-3,6-disulphonic acid "H-acid" (0.0025 moles, 0.99g) was dissolved in 20 ml sodium carbonate solution (2%, pH=14) and then added dropwise in to the stirring solution of diazonium salt (0.0025 moles). The solution was maintained at pH 8. The coupling was sustained for 1 hour at 0-5ºC [14].

2.3.3 Metallization

The pH was lowered to 4 by adding sodium acetate at 45-50ºC. Into the stirring solution 0.00125 moles of Cr $(CH_3COO)_2.H_2O$ (0.2124g) was added. Heating was continued until there was no differentiation on the chromatogram which was eluted by 1% NaCl solution. After one and half an hour 10% NaCl solution was added this resulted in salting out. The metal dye complex was separated and then dried in oven. In the same way other metal salts such as $FeSO_4.7H_2O$ (0.4675g), $Co(NO_3)_2.6H_2O$ (0.3575g), $CuSO_4.5H_2O$ (0.2919g) were added in separate reaction mixture and resulting metal dyes complexes were collected. These were then subjected to spectroscopic analysis [14].

2.4 Synthesis of metal complexes of sodium [8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3'-sulfo phenyl azolyl) 3,6-disulphonate].

General procedure

2.4.1 Diazotization

3-amino-1-hydroxy-5-nitro benzene sulphonic acid (0.0025 moles, 0.45g) was dissolved in 15-20 ml HCl (30%) at room temperature. The solution was then cooled to 0-5 ºC in an ice bath and maintained at this temperature, solution of sodium nitrite (0.0025 moles, 0.17g) in water (10-15 ml) was added dropwise within 20 minutes under continuous stirring and the mixture was stirred at 0-5ºC for 1 hour.

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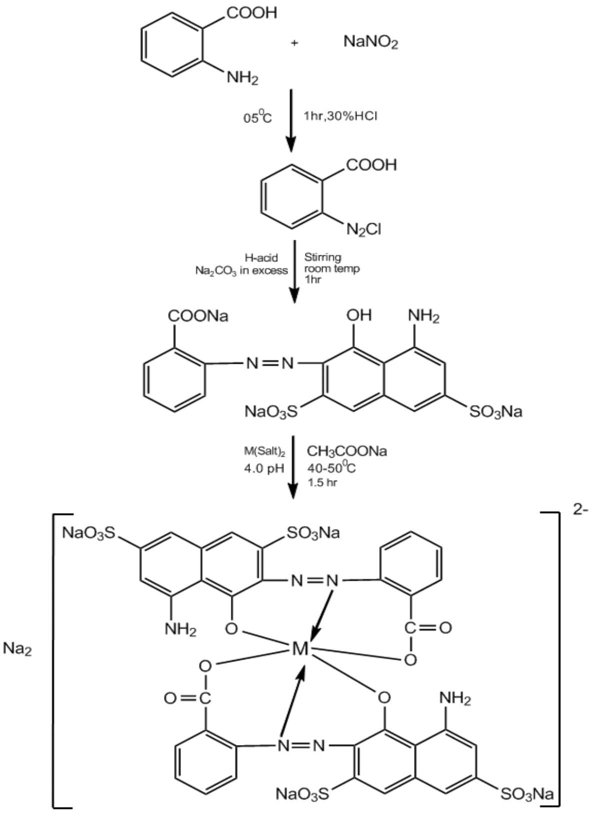
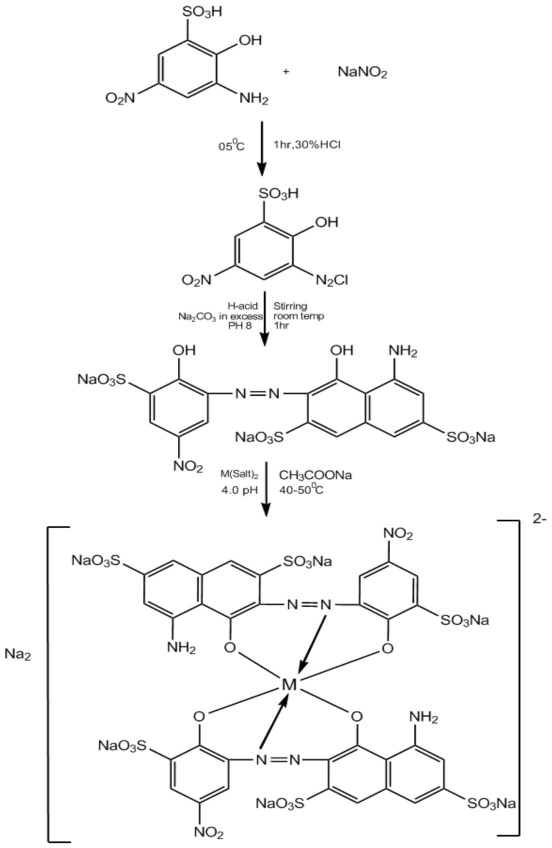


M- Salts: Cr $(CH_3COO)_2.H_2O$, $FeSO_4 .7H_2O$, $Co(NO_3)_2.6H_2O$, CuSO4.5H_2O

Scheme 1: Synthesis of metal complexes of anthranillic acid dyes using H-acid as coupler



M- Salts: Cr $(CH_3COO)_2.H_2O$, $FeSO_4 .7H_2O$, $Co(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$

Scheme 2: Synthesis of metal complexes of 4-napsa dyes using H-acid as coupler

3. RESULTS AND DICUSSION

Metal complex of azo dyes with general formula ML_1 and ML_2 [Where M= Cr(II), Fe(II), Co(II), Cu(II), L_1=($C_{17}H_{12}O_6N_3S_2$) and L_2= ($C_{16}H_{11}O_{10}N_4S_3$)] were prepared by reaction of appropriate metal salts, $Cr(CH_3COO)_2$, $FeSO_4.7H_2O$, $Co(NO_3)_2.6H_2O$, $CuSO_4.5H_2O$ with sodium[8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate] (L_1) and sodium[8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3-sulfo phenylazolyl) 3,6-disulphonate] (L_2) in 1:2 molar ratio respectively. The physical data of azo dyes and their respective metal complexes were shown in Table 3.1 and Table 3.2. Such metal complexes of azo dyes were characterized by UV-visible spectroscopy and FT-IR.

3.1 UV-Visible studies of the dyes.

Absorption spectra of azo dyes sodium [8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate] (L_1) and sodium[8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3-sulfo phenylazolyl) 3,6-disulphonate] and their metal complexes were recorded in H_2O and the results were summarized in Table 3.3 and Table 3.4. The color of these azo dyes depends on the nature of the diazo and the coupling components. The additional color shifts, that is shifting of λ_{max} toward higher wavelength (bathochromic shift) or lower wavelength (hypsochromic shift) are due to presence of electron donating or electron attracting group in the coupler moiety. The band in the region 590-620 nm in H_2O is the electronic spectra of these dyes. This band was due to electronic transition relating the whole conjugated system. The absorption band produces hypsochromic shift due to the presence of carboxyl group as an electron withdrawing substituent on to the ring. This was observed for the azo dye where the introduction of the carboxyl as an electron acceptor resulted in the bathochromic shift 50-60 nm, as compared with the hydroxyl group in the diazo component of azo dye. The introduction of Cr(II) in the dye (λ_{max}=600 nm) resulted in the hypsochromic shift of 10 nm compared to the dye (λ_{max}=590 nm) while the same effect is observed by the introduction of Co(II) and the Cu(II) in the dye resulted in hypsochromic shift of 90 nm and 30 nm respectively. And the introduction of Fe(II) only shift (bathochromic) 90 nm compared to the dye . This is attributed to the smaller steric requirements of the rod like COOH group and the more electron delocalization system. The nature of the coupling site as well as the nature of the substituents at the terminal phenyl group dictates the change in the λ_{max} value.

The absorption maxima values (λ_{max}) are directly comparative to the electronic power of substituents in the coupler ring system. The presence of electron donating or electron attracting group in the coupler moiety results in additional color shifts, that is (λ_{max}) towards higher wavelength (bathochromic shift) or lower wavelength (hypsochromic shift) respectively, (PATEL, 2011). The introduction of Cr(II) in the dye (620 nm) resulted in the bathochromic shift of 60 nm compared to the dye (λ_{max}=680 nm), The same effect is observed by the introduction of Co(II) and Cu(II) in the dye resulted in the bathochromic shift of 200 nm and 80 nm respectively. And the introduction of Fe(II) only shift 2 nm compared to the dye as shown in Table 4.4. This is all due to much decreased electron density on the metal ligands. This is attributed to the smaller steric requirements of the rod like nitro group and more electron delocalization system. The data revealed that the change in the λ_{max} value depends upon the nature of the coupling site and nature of the substituents at the terminal phenyl group. This is in agreement with that previously reported by (PATEL et al, 2011). Meanwhile, on comparing azo dyes the substituents on the phenyl ring of diazonium site exerted a negligible change in λ_{max}.

Table-3.1: Physical properties of sodium [8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate] and it metal complexes.

Compound no.	Molecular Formula	Physical state	Melting point (Fusion)	Solubility in H_2O
1	$C_{17}H_{12}O_6N_3S_2$	solid	325ºC	soluble
2	$(C_{17}H_{12}O_6N_3S_2)_2Cr$	solid	501ºC	soluble
3	$(C_{17}H_{12}O_6N_3S_2)_2Fe$	solid	490ºC	soluble
4	$(C_{17}H_{12}O_6N_3S_2)_2Co$	solid	524ºC	soluble
5	$(C_{17}H_{12}O_6N_3S_2)_2Cu$	solid	540ºC	soluble

Table-3.2: Physical properties of sodium [8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3-sulfo phenylazolyl) 3,6-disulphonate].

Compound no.	Molecular Formula	Physical state	Melting point (Fusion)	Solubility in H_2O
1	$C_{16}H_{11}O_{10}N_4S_3$	solid	340ºC	soluble
2	$(C_{16}H_{11}O_{10}N_4S_3)_2Cr$	solid	510ºC	soluble
3	$(C_{16}H_{11}O_{10}N_4S_3)_2Fe$	solid	496ºC	soluble
4	$(C_{16}H_{11}O_{10}N_4S_3)_2Co$	solid	536ºC	soluble
5	$(C_{16}H_{11}O_{10}N_4S_3)_2Cu$	solid	560ºC	soluble

Table 3.3: λ_{max} of light absorbed in nm of $^*MC_{34}H_{24}O_{12}N_6S_4$.

Compound no.	Molecular Formula	λ_{max}(nm)	Observed color
1	$C_{17}H_{12}O_6N_3S_2$	530	Bluish red
2	$(C_{17}H_{12}O_6N_3S_2)_2Cr$	530	Bluish red
3	$(C_{17}H_{12}O_6N_3S_2)_2Fe$	530	Bluish red
4	$(C_{17}H_{12}O_6N_3S_2)_2Co$	530	Bluish green
5	$(C_{17}H_{12}O_6N_3S_2)_2Cu$	530	Violet blue

Table-3.4: λ_{max} of light absorbed in nm of $^*MC_{32}H_{22}O_{20}N_8S_6$.

Compound no.	Samples	λ_{max}(nm)	Observed color
1	$C_{16}H_{11}O_{10}N_4S_3$	570	Bluish green
2	$(C_{16}H_{11}O_{10}N_4S_3)_2Cr$	430	Greenish blue
3	$(C_{16}H_{11}O_{10}N_4S_3)_2Fe$	400	Bluish green
4	$(C_{16}H_{11}O_{10}N_4S_3)_2Co$	400	Brown
5	$(C_{16}H_{11}O_{10}N_4S_3)_2Cu$	490	Blue

*M=Cr(II), Fe(II), Co(II), Cu(II).

3.2 Infra-Red studies

The IR-spectral data of dyes and their metal complexes is shown in Table 3.5 and 3.6. The assignment of different functional groups made on according to the literature value. Three strong O-H absorptions are observed in the region of 3074-3558 cm^{-1} in the spectra of metal complexes of Fe(II), Co(II) and Cu(II). Due to hydrogen bonding the O-H absorption band, appearing in the spectra of metal free ligands is not observed (GUP, 2007). The band at 3321-3437 cm^{-1} region corresponding to N-H stretching vibrations of primary amino group and another band at 1436-1600 cm^{-1} region is due to N=N stretching vibration of azo group as shown in scheme 1. Moreover a band due to –N=N- at 1436-1600 cm^{-1} in the spectra of all metal dye complexes indicating coordination. sodium[8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate] showed C=O stretching vibration at 1789 cm^{-1} while metal complex and their types showed C=O stretching at 1600-1680 cm^{-1}, which confirmed the formation of benzoate linkage via conversion of carboxyl to carboxylate metallized ring. The C=O absorption band appearing in the spectra of metal free ligand at 1789 cm^{-1}. The introduction of Cr(II) and Co(II) shift the spectra towards strong field due to coordination and decreased electron density on ligand atoms, while reverse happens by introducing Fe(II) at 1867 cm^{-1} because it acts as electron donator, the electron density at ligand atom was not decreased. A new band due to C-O vibrations appears roughly 1230-1298 cm^{-1} indicating the co-ordination between metal and ligand in the (spectra) of all metal dye complexes. Other distinguishing band of all the dyes appearing at 1219-1400 cm^{-1} are due to asymmetric and symmetric S=O stretching of sulphonic acid group, 1230-1581cm^{-1} are due to asymmetric and symmetric N=O stretching of nitro group [15]. In sodium [8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3-sulfo phenylazolyl) 3,6-disulphonate] the first absorption band which is appearing in the spectra of metal free ligands at 3516 cm^{-1}. Because of hydrogen bonding, metal complex of Cr(II) has no O-H peak, Fe(II) and Co(II) complexed dyes showed O-H stretching at 3261-3516 cm^{-1} correspondingly. The band corresponding to N-H stretching vibrations of primary amino groups appearing at 3290 cm^{-1}-3442 cm^{-1} region as shown in scheme 2. Azoic group gives band at 1458 cm^{-1}-1650 cm^{-1} due to -N=N- stretching vibration. The spectra of all metal dye complexes indicating coordination giving bands due to –N=N- in the region of 1458 cm^{-1}-1650 cm^{-1}. Because of the absence of the group (C=O) from the metal free ligand metal dye complexes showed no C=O stretching vibrations. In the spectra of all metal dye complexes indicating coordination a new band due to C-O vibrations appeared around 1172 cm^{-1}-1222 cm^{-1}. Other distinguishing bands of all the dyes appearing at 1369 cm^{-1}-1404 cm^{-1} are due to asymmetric and symmetric S=O stretching of sulphonic acid group, similarly absorption at 1396 cm^{-1}-1674 cm^{-1} are due to asymmetric and symmetric N=O stretching of nitro group [15].

3.3 Antibacterial studies

For the antibacterial and antifungal activity (DDM) in vitro by broth dilution method with two gram-positive bacteria S.aureus, P.multocida and two gram-negative bacteria E. coli, B. subtilis and fungi Alternaria, G. lucidum organisms taking rephempicin and fluconazol as standared drug, were tested against all the synthesized dyes.

Very good activity against E.coli and good activity against S.aureus with respect to standared drug rephempicin were shown by all dyes. The growth of bacteria was inhibited which attributed to fact that presence of azo, phenyl and naphthyl groups [16]. Antibacterial data were summarized in Table 3.7.

3.4 Application of metal complex dyes on fabrics

The citadel property of all the dyes rating 3-4 for cotton shows that it ranges from moderate to good except Cr(II) and Co(II) whose rating is 2-3. The wash citadel and chafing properties of all the dyes rating 4-5 except Cr(II) and 3-4 respectively for cotton show that these properties of all the dyes range from moderate to good. It means that the introduction of Cr(II) and Co(II) have not convinced to be good mordants. The good wash citadel properties may be due to the better dye invasion and good covalent fixation with the fabrics. The solubility of the dyes and rate of movement of dyes out of the fiber during washing depends on the (size of the dye molecule) and also on the (nature) and (position of substituent) present on the coupler ring. In case of dyes of 4-napsa light citadel properties were in rating 4 except Cr(II) and Cu(II) whose rating was 2 and 2-3 correspondingly. Fe(II) gave excellent chafing properties. The data of light, sluice and chafing citadel properties of all the dyes are shown in Table 4.8 and 4.9 respectively.

3.5 Colorimetric studies (CIE lab values)

The color of a dye on cotton is expressed in terms of CIE (color index exhaustion) lab values Table 3.10 and 3.11 show following CIE lab co-ordinate were measured, lightness (l*), chroma (C*), hue angle from 0°-180° (h*), b* represents the degree of yellowness (positive) and blueness (negative) and a* value represents the degree of redness (positive) and greenness (negative). On the dyed sample a reflectance spectrophotometer was used for the colorimetric measurements. According to the Kubelka-Munk equation K/S values given by the reflectance spectrophotometer are designed with respect to λ_{max} and are directly correlated with the dye concentration on the substrate [17].

$K/S= (1R)^2/2R$

Where R is the reflectance ratio and K is the absorbance coefficient. All dyes were reddish, except A_4 which is greener due to Cu(II). Similarly A_1 and A_3 are bluer, A_2 and A_4 are yellow all exhibiting lighter shade. The dye A_3 had the highest value of color strength difference 14.41. Due to increased substantivity, the cotton fibers possess highest K/S than other dyes [19]. Other dyes are reddish, except B_3 which is brownish due Co(II). However all are bluer lighter except B_3 which is darker. The dye B_1 has the highest value of color strength of 32.57. Here due to increased substantivity fibers also possess highest color difference than other dyes.

Table-3.5: IR absorption frequencies in cm^{-1} of *$M(C_{17}H_{12}O_6N_3S_2)_2$.

Serial.no	**Functional group description**	**Observed wavenumber (cm^{-1}) of metal dyes complexes of anthranillic acid (H-acid as coupler)**				
		Compound No 1	**Compound No 2**	**Compound No 3**	**Compound No 4**	**Compound No 5**
1	OH Stretch	-	3140	3558	3074	3425
2	NH	3390	3350	3437	3240	3321
3	Ar-H	3049	3140	3088	3074	3196
4	C=O	1789	1616	1867	1674	1763
5	N=N	1436	1600	1570	1595	1436
6	N=O	1579	1230	1242	1450	1581
7	S=O	1255	1400	1363	1219	1309
8	C=O	1266	1230	1242	1298	1240

Table-3.6: IR absorption frequencies in cm^{-1} of *$M(C_{16}H_{11}O_{10}N_4S_3)_2$.

Serial no.	**Functional group description**	**Observed wavenumber (cm^{-1}) of metal dyes complexes of 4-NAPS (H-acid as coupler)**				
		Compound No 1	**Compound No 2**	**Compound No 3**	**Compound No 4**	**-----------**
1	OH Stretch	-	3516	3442	3261	--------
2	NH	3336	3320	3442	3290	--------
3	Ar-H	2945	3124	3074	3190	--------
4	S=O	1371	1369	1394	1404	--------
5	N=N	1458	1483	1650	1157	--------
6	N=O	1396	1587	1674	1558	--------
7	C=O	1172	1222	1219	1220	--------

*M= Cr (II), Fe (II), Co (II) and Cu (II).

Table-3.7: Antibacterial activity of metal complex dyes of Cr(II), Fe(II), Co(II), Cu(II) against selected bacterial strains.

Compound no	S.Areus	E. Choli	P.Multocida	B.Sustilis
A	-	30	-	18
A_1	-	-	-	14
A_2	20	-	12	20
A_3	18	18	-	-
A_4	20	16	-	20
Control Rephempicin	28	30	24	-
B	18	18	12	22
B_1	14	-	-	14
B_2	14	20	24	12
B_3	18	16	18	-
B_4	18	-	-	20
Control Rephempicin	30	26	22	-

The value in the table are the mean of three independent experiments in mm
(-) No activity/poor activity
(+) Bacterial strains used are

(i) Staphylococcus areus
(ii) Escherchia choli
(iii) Pasturella multocida
(iv) Bacillis subtilis

Table-3.8: Fastness properties of *M$(C_{17}H_{12}O_6N_3S_2)_2$

Sample No.	Molecular formula	Rubbing Test		Washing Test		Light fastness
		Dry Test	Wet Test	Change in shade	Stain	
1	$C_{17}H_{12}O_6N_3S_2$	4-5	3-4	2-3	4-5	3-4
2	$(C_{17}H_{12}O_6N_3S_2)_2Cr$	4-5	3-4	1-2	4-5	2-3
3	$(C_{17}H_{12}O_6N_3S_2)_2Fe$	4-5	3-4	1-2	3-4	3-4
4	$(C_{17}H_{12}O_6N_3S_2)_2Co$	4-5	3-4	1-2	3-4	3-4
5	$(C_{17}H_{12}O_6N_3S_2)_2Cu$	4-5	4-5	2-3	4-5	3-4

Table-3.9: Fastness properties of *M$(C_{16}H_{11}O_{10}N_4S_3)_2$.

Sample No.	Molecular formula	Rubbing Test		Washing Test		Light fastness
		Dry Test	Wet Test	Change in shade	Stain	
1	$C_{16}H_{11}O_{10}N_4S_3$	4-5	2-3	1-2	4-5	2-3
2	$(C_{16}H_{11}O_{10}N_4S_3)_2Cr$	4-5	2-3	2-3	3-4	4-5
3	$(C_{16}H_{11}O_{10}N_4S_3)_2Fe$	4-5	3-4	2-3	2-3	4-5
4	$(C_{16}H_{11}O_{10}N_4S_3)_2Co$	4-5	2-3	4-5	4-5	4-5
5	$(C_{16}H_{11}O_{10}N_4S_3)_2Cu$	4-5	2-3	1-2	3-4	2-3

*M= Cr(II), Fe(II), Co(II), Cu(II)
Light fastness: 1, poor; 2, moderate; 3, good; 4, very good; 5, excellent.
Wash and rubbing fastness: 1, poor; 2, fair; 3, good; 4, very good; 5, excellent.

Tabl-3.10: colorimetric studies of *M$(C_{17}H_{12}O_6N_3S_2)_2$.

Dye sample	Molecular Formula	l*	a*	b*	c*	H	DE
A_1	$(C_{17}H_{12}O_6N_3S_2)_2Cr$	-6.54	5.46	-4.5	6.60	-2.57	9.63
A_2	$(C_{17}H_{12}O_6N_3S_2)_2Fe$	-3.39	1.32	3.23	0.83	3.39	4.86
A_3	$(C_{17}H_{12}O_6N_3S_2)_2Co$	-11.15	8.10	-4.23	8.97	-1.71	14.41
A_4	$(C_{17}H_{12}O_6N_3S_2)_2Cu$	-1.33	-6.92	2.65	-7.32	1.17	7.53

Table-3.11 colorimetric studies of *M $(C_{16}H_{11}O_{10}N_4S_3)_2$

Dye sample	Molecular Formula	l*	a*	b*	c*	H	DE
B_1	$(C_{16}H_{11}O_{10}N_4S_3)_2Cr$	-12.06	7.72	29.26	13.30	27.18	32.57
B_2	$(C_{16}H_{11}O_{10}N_4S_3)_2Fe$	-5.98	7.17	29.58	13.36	27.35	31.02
B_3	$(C_{16}H_{11}O_{10}N_4S_3)_2Co$	23.93	-1.39	12.54	-5.97	11.27	27.05
B_4	$(C_{16}H_{11}O_{10}N_4S_3)_2Cu$	-6.44	20.68	7.96	13.79	17.35	23.08

*M= Cr(II), Fe(II), Co(II), Cu(II)

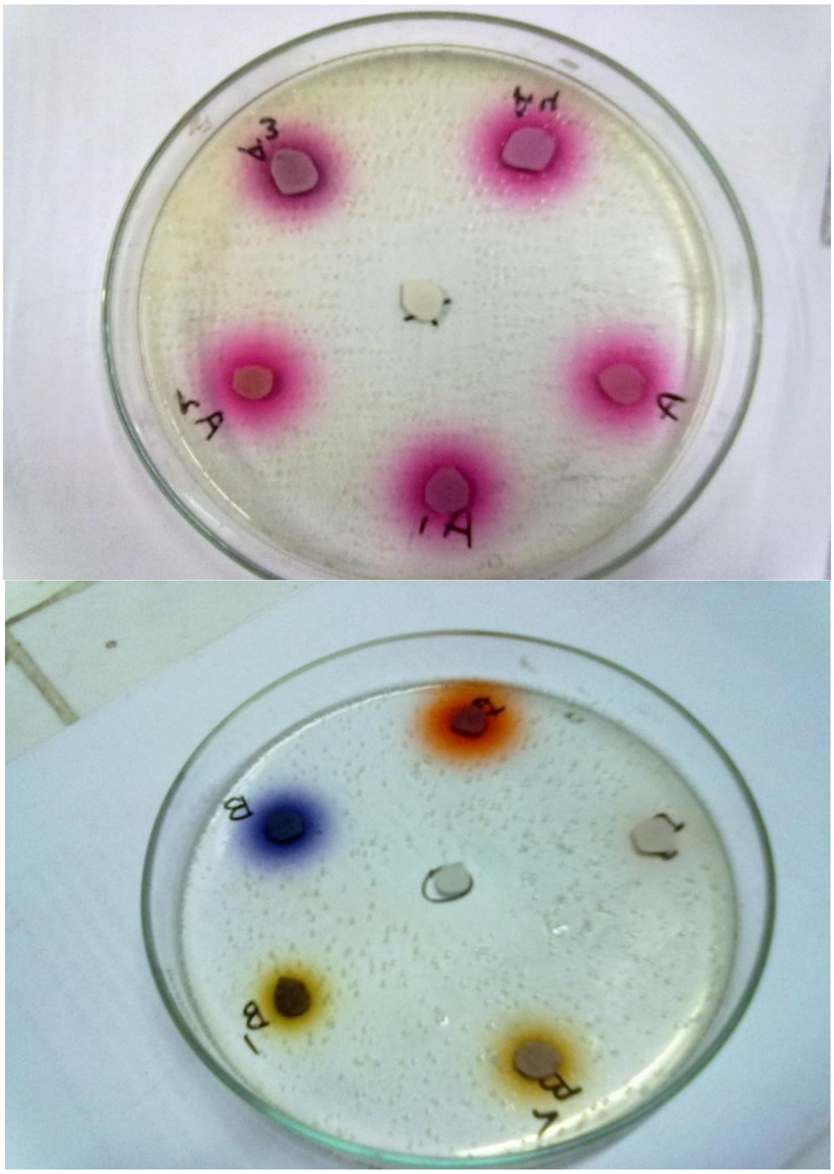


Fig-1: Anti-Bacterial Activity on S.A

CONCLUSION

A series of monoazo o'o hydroxy metal complexed direct dyes based on sodium [8-amino-1-naphthol-2(2'-carboxy phenylazolyl 3,6-disulphonate] and sodium[8-amino-1-naphthol-2(2'-hydroxy-5'-nitro-3-sulfo phenylazolyl) 3,6-disulphonate] have been prepared by the process of direct diazotization and couplig in valuable yield. These dyes have good compatibility with fabrics due to very good percentage (exhaustion and fixation) of these dyes. The light, sluice and chafing citadel properties of these dyes were good, this indicated that these dyes have good substantivity with fabrics. The physical properties, spectral properties, antimicrobial activity properties have been evaluated and proposed to be studied regarding as follows.

I. Synthesis of (mono azo dyes) along with their metallization process was studied.
II. The study of spectroscopic aspects like UV-Visible and FT-IR.
III. The study antimicrobial activity of the metallized dyes.
IV. The study of their application on cotton.

After studying the synthesis and characterization following factors dictated that dyes are also

1. Temperature sensitive
2. pH sensitive

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