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Complexation Trends And Biological Activity Of Some Mixed Ligand Complexes Of Curcumin And 1:10-Phenanthroline With Selective Metal Ions.

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ABSTRACT

Mixed metal ligand complexes is reported with Curcumin (CUM) as a primary ligand and 1:10-phenanthroline (phen) as secondary ligand. The structures of these complexes are confirmed by using FT-IR and UV- electronic spectroscopies, magnetic moments, melting points , molar conductivity measurements .and the metal % analysis revealed that the complexes analyze indicates a six coordinated as[M(CUM)(Phen)$_2$]Cl, M=Mn (II), Co(II), Ni(II),Cu(II) ,Zn(II) , Cd(II) , Hg(II) and [M' (CUM)(Phen)$_2$]Cl$_2$ M'= Cr(III) &. Fe(III). In-vitro antimicrobial studies on (Curcumin and 1:10-phenanthroline ligands and mixed metal ligand complexes against {(Bacillus subtilis (G+) , Esherichia Coli (G-) and as well as antifungal activities against Candida albicans by measuring the zone of inhibition in mm. The investigation includes the produced dyes were applied of Cotton without Mordant.

Keywords: Curcumin, 1:10-phenanthroline, antimicrobial activity, dyes and complexes.

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INTRODUCTION

Many research papers have been published on preparing of metal complexes with mixed ligands and characterization (1–2).

Curcumin, ;polyphenol a hydrophobic yellow-orange derived from the rhizome of the herb Curcuma longa, used in pharmaceutical preparations and food(3–4) exhibit many beneficial health effects including its ant carcinogenic. (5).

Many studies have shown that 1:10-Phenanthroline is good started material for obtaining heterocyclic compounds and is one of the best compound used in many reactions. (6)

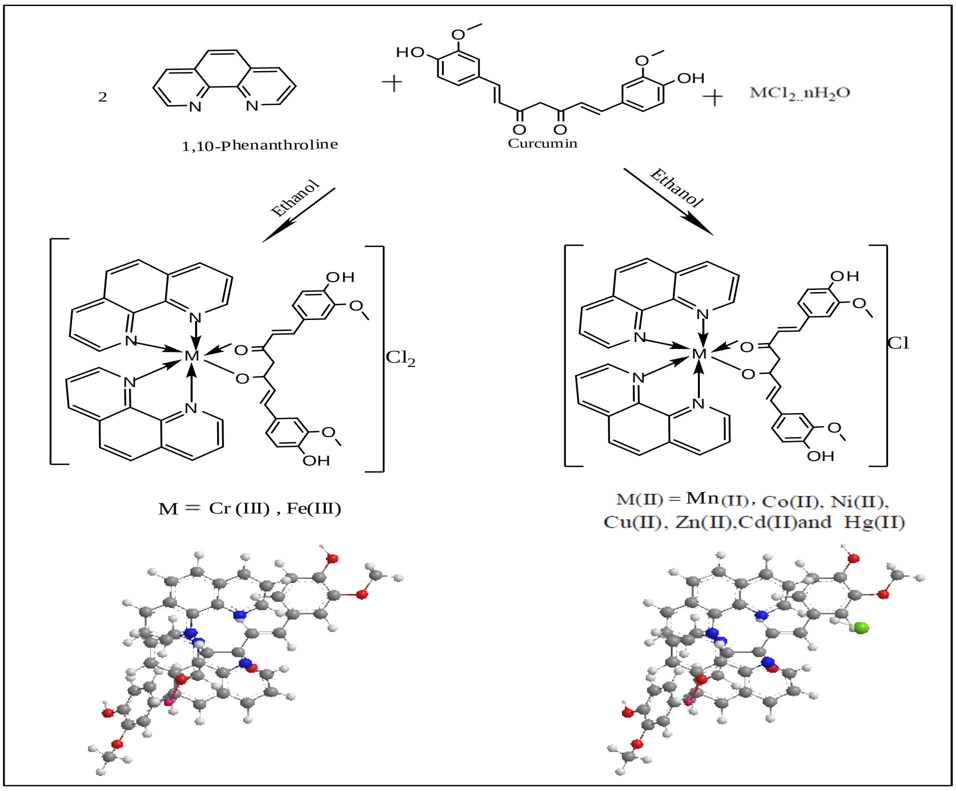
1 ,10-phenanthroline was synthesized by Fritz Blauin In1898,and use it to prepared Ni(II) Fe(II), ,co(II) and Cu (II) complexes and was able to recognize them as Werner coordination compounds (7-8)

$[Cu\ (phen)_2]cl\ _2$ was discovered to have nuclease activity(9).The uses anti-*Candida* potential of (Mn(II), Cu (II), and Ag(I)) phen -chelates evaluate different for their ability to inhibit planktonic growth and biofilm of *C. haemulonii* species complex. (10)

In this paper, we have been undertaken in order to get information on the structure of the Mixed Ligand Complexes Of Curcumin And 1:10-Phenanthroline With Bivalent Metals Chlorides using FT-IR, UV-Visible and molar conductance The physicochemical and antimicrobial Activities study of this complexes should therefore be a good candidate to study and characterize. This is the theme of this work.

EXPERIMENTAL

All the chemicals and solvents were purchased of A.R. Grade quality obtained from (Aldrich and BDH) were used without further purification. All complexes were prepared in general procedure (11) are schematically presented in scheme 1 .



Scheme 1: The synthesis route of Metal Mixed Ligand Complexes

RESULTS AND DISCUSSION

The complexes were prepared by reacting the respective metal Chloride with the ligands using 1:1:2 mole ratios, [CUM:M:2Phen], i.e. one mole of Curcumin[CUM], one mole of metal Chloride and two moles of 1,10-Phenanthroline [Phen].The formula weights and melting points are given in Table (1). It was found that all the complexes were appeared as powders and stable in air at room temperature with higher melting points revealing that the complexes are much more stable than their parent ligands indicating formation of complexes, (11). The solubility of the complexes in the seven solvents (H_2O,aceton ,benzene, methanol, ethanol, hexane and DMSO) used, varied according to metals used: All complexes were insoluble in benzene, hexane, water, and soluble in all the solvents under study . The molar conductivity

(ohm^{-1}.cm^{2}.mol^{-1}) of all complexes solutions measurements (1 x 10-3 M in DMSO as solvents , the values shown in Table 1 . values reveal the existence of exhibit an electrolytic nature type 1:1 for Mn (II), Co(II), Ni(II), Cu(II) ,Zn(II) , Cd(II) , and Hg(II) . type 1:2 for Cr(III) and Fe(III) . (12)

Table 1: Some Physical properties of the compounds

Compounds Chemical Formula)	M. wt Calc.	Colour	Yield %	M .p°c (de) °c	n Ω^{-1} cm^{2} mol^{-1}	Metal% (exp)
[Cr(CUM)(Phen)2]Cl2	852.70	Deep Brown	58	> 260.	59.5	6.10 (5.84)
[Fe(CUM)(Phen)2]Cl2	856.55	Deep Brown	50	246	60.1	6.52 (4.98)
[Mn(CUM)(Phen)2]Cl	835.22	Yellow	50	> 260	42.1	6.58 (7.32)
[Co(CUM)(Phen)2]Cl	839.22	Brown	69	199	34.5	7.02 (5.59)
[Ni(CUM)(Phen)2]Cl	838.98	Orang	70	206	42.4	7.00 (6.07)
[Cu(CUM)(Phen)2]Cl	843.83	Deep Green	60	244	43.9	7.53 (9.82)
[Zn(CUM)(Phen)2]Cl	845.70	Yellow	52	> 260	30.6	7.73 (5.26)
[Cd(CUM)(Phen)2]Cl	892.70	Yellow	57	> 260	36.6	12.59 (10.99)
[Hg(CUM)(Phen)2]Cl	980.88	Yellow	50	> 260.	30.6	20.45 (19.17)

All of the complexes in this paper are paramagnetic except [Zn(II),Cd(II),& Hg(II)].

The electronic spectra of all the complexes solutions under study were recorded in (10-3 M) in (DMSO) at room temperature .The UV and visible data and magnetic moments (μef)of compounds are summarized in table-2.The (U.V-Vis)spectrum for the (CUM) exhibits two intense bands at (λmax 268 nm)(37313 cm-1) which is assigned to (π→π*),and (λmax 434 nm)(23041cm-1)which are assigned to(n→π* transitions .in the ketone (C=O) group. Thus, the π-π* and n-π* absorptions of (CUM) move close to each other agree with data reported by several research workers , (14-16). A observed a shift in positions of these bands is when these-Keto - compounds are engaged in complex formation with metals through –C=O group. Apart from these bands some specific bands are also observed in case of all complexes which are listed as below in Table 3. The (U.V-Vis) spectrum for the (phen)exhibits absorption peak at (λmax 289 nm)(34602cm^{-1}) is assigned to (π→π*),transition (16). Electronic spectra and magnetic moment of the complexes confirmed the octahedral geometry for the complexes. The spectrum (υ, cm-1) for (CUM) recorded strong band at (3444) cm1- which a signed to hydrogen bonded υ(OH) phenolic and a peak at 2480 cm^{-1} due to asym. ν(C-O-C) stretching, also, an additional peak at 10268 cm^{-1} , owing to sym ν (C-O-C) stretching, a distinct peak for ν (Ar-O-CH3)recorded at 1254 cm-^{1} and 1469, cm^{-1} ν (C=C) str ,841 cm^{-1}out of plain ν (C-H benz.) (17-18).The spectrum of 1:10-phenanthroline is quite similar, the one band occurring at 1504 cm $^{-1}$, the second appearing as a triplet with the center component at 1589 cm $^{-1}$ and the third band shifting to 1419 cm -1. Reference has been made previously to the fact that all these bands move to higher frequencies on coordination. And band at 3059 cm $^{-1}$ due to vCH stretching وThe spectra of (phen)and its complexes in general were complicated. (19-22).The absence of a strong band near 1500 cm $^{-1}$ suggests that this particular ring frequency in the (phen)compound. involving υ (C — C) & υ (C — N) stretching .This is quite expected as the coordination takes place at (N) and the effect is transmitted throughout the region resulting into the readjustment of a electron density. The least sensitive of these vibrations appears to be one at 1418 c m $^{-1}$ as reported by literature (20).The (CUM) ligand coordinates in bidentate fashion via its two keto (C=O) moieties. The study supported that the metal ion in all the complexes have hex coordinated and the complexes had octahedral geometries (Scheme-1).

Table 2: Electronic spectral Data of compounds

Comp.	Nm	υ' cm-1	Є max mol^{-1}.L.cm^{-1}	Assignments	μeff B.M
[Cr(CUM)(Phen)2]Cl2	272 437 786 865	36764 22883 12722 11560	1889 2151 10 10	ligand field charge transfer 4A2g→4T1g(P) v3 4A2g→4T1g v2	3.74
[Fe(CUM)(Phen)2]Cl2	279 443 649	35842 22573 15408	1406 1701 85	ligand field charge transfer 6A1g(S) →4T1g	5.99
[Mn(CUM)(Phen)2]Cl	282 429 452 828	35460 23310 22123 12077	1586 229 198 7	L.F Charge transfer 6A1g(S) →4T1g (υ3) 6A1g(S) →4T2g (υ2)	5.87
[Co(CUM)(Phen)2]Cl	271 433 836	36900 23094 11961	1710 1937 26	L.F Charge transfer 4T1g(F) → 4A2g(F)	4.5 1
[Ni(CUM)(Phen)2]Cl	272 435 982	36764 22988 10183	1919 2339 65	L.f C-T 3A2g(F) → 3T1g(F)	2.91
[Cu(CUM)(Phen)2]Cl	279 438 462 829	35842 22831 21645 12062	1352 1549 1535 2	C-T C-T C-T 2Eg →2T2g	2.07
[Zn(CUM)(Phen)2]Cl	281 430 452	35587 23255 22123	1498 633 568	Charge transfer π→π* π→π*	Diamag.
[Cd(CUM)(Phen)2]Cl	272 427	36764 23419	1873 140	Charge transfer π→π*	Diamag.
[Hg(CUM)(Phen)2]Cl	281 435	35587 22988	1541 900	Charge transfer π→π*	Diamag.

Table 3: Assignment of infrared frequencies in Cm-1of the (CUM)

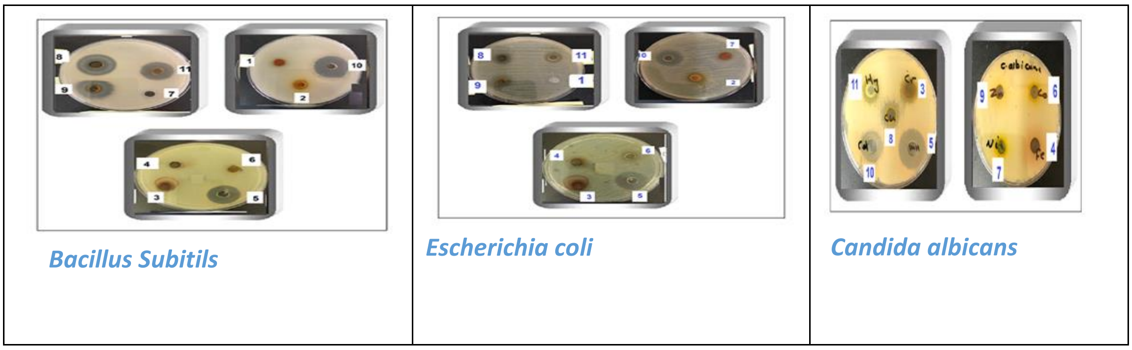
Phenolic υ(OH)	υ(C-H) aromatic	υ(C-H) aliphatic	υ(C=O)	υ(C=C)	(Ar-C=C)	υ (C-O-C)	υ(-OCH3)
3444	3066	2935	1597	1454	1438	1157	1133

Table 4: Assignment of infrared frequencies in Cm^{-1} of the [CUM-M-phen] complexes

Compound	Phenolic υ(OH)	υ(C-H) aromatic	υ(C-H) Aliphatic	υ(C=O)	υ (C=C)	υ (C-N)	υ N)	υ O)
[Cr(CUM)(Phen)2]Cl2	3425	3070	2970	1624 1377	1593	1427	543	435
[Fe(CUM)(Phen)2]Cl2	3429	3066	2966	1624 1369	1593	1427	509	428
[Mn(CUM)(Phen)2]Cl	3414	3047	2993	1620 1373	1585	1423	543	443
[Co(CUM)(Phen)2]Cl	3387	3001	2966	1624 1373	1581	1423	509	428
[Ni(CUM)(Phen)2]Cl	3390	3061	2958	1631 1427	1585	1427	520	416
[Cu(CUM)(Phen)2]Cl	3317	3016	2835	1620 1369	1585	1427	520	428
[Zn(CUM)(Phen)2]Cl	3425	3055	2927	1624 1427	1585	1427	547	424
[Cd(CUM)(Phen)2]Cl	3425	3047	2997	1620 1427	1585	1427	559	428
[Hg(CUM)(Phen)2]Cl	3425	3055	2997	1624 1427	1589	1427	509	424

Antibiological and antifungal Evaluation

The study of biological activity of the studied ligands and their metal complexes against bacteria and fungi showed selectivity nature of microorganism towards these compounds, effect of metal ion on activity of ligands as well as nature of ligands. which can be attributed to the complexation of the metal ions with the donor atoms of the ligand. In keeping with Tweedy conception (19- 22) these strongly bound metal complexes may prove to be better antimicrobial agents, binding them to the bacterial cell walls These results indicated the possibility of using some of these mixed ligand complexes as antibacterial and antifungal agents. Figure.1 and **Scheme (2)**



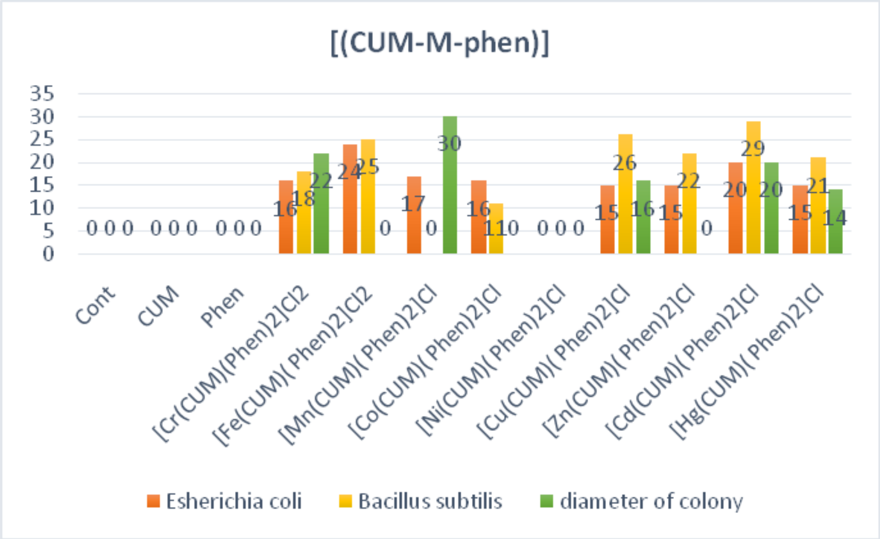
Bacillus Subitils

Escherichia coli

Candida albicans

Figure 1: Photograph of biological activity of mixed

[(CUM) - Metal– $(phen)_2$] complexes



Scheme (2): Chart of biological effects of the studied compounds

Evaluation of color fastness properties

Wash fastness of the samples dyed under the optimized conditions is tested according to ISO 105-CO3 method. After dyeing, the dyed samples are rinsed with water and ethanol , washed in a bath with a liquor ratio of 1:50 using 1 gm/liter of the soaping agent at 700C for 15 minutes and then they are rinsed and finally dried

Dyeing bath (Beeker) for sample was prepared by only a natural dye and required dyeing auxiliaries as wetting agent (ethanol and drops of acetic acid).The result showed that the color fastness rating of the cotton fabric. The best results with respect to time for dyeing cotton fabrics are obtained at 15 minutes. It is also seen that the effect of different complexes on color strength of cotton fabric are not same.

Properties porous structure and capillaries in fully developed cotton should have free flow of liquor during dyeing. The wash fastness rating of cotton fabric dyed with acid is presented in table (5) and figures (2-3).and compared Fastness level figure (4) rubbing fastness ratings and chanced color .

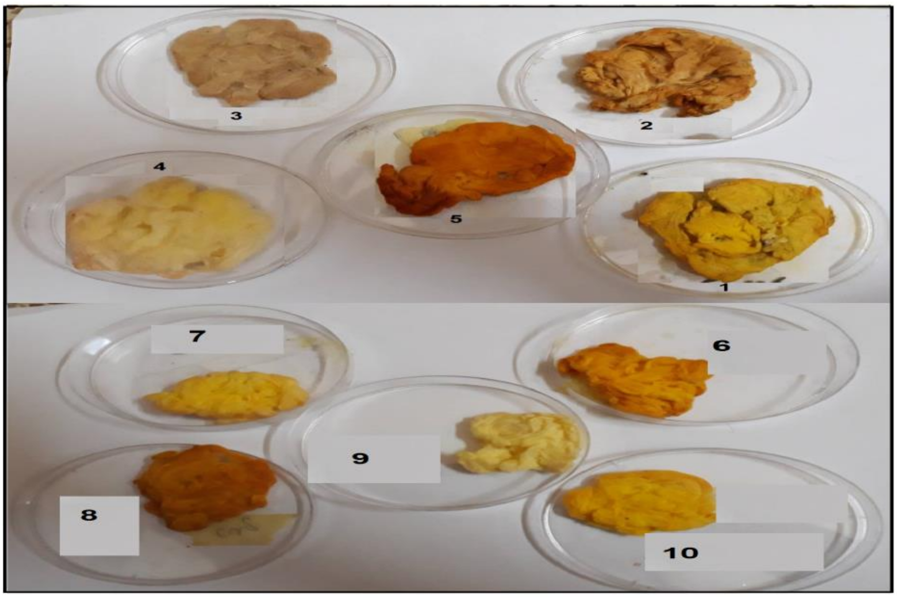


Figure 2: Samples of cotton tissue dyeing by Mixed [CUM- Metal- Phen] Complexes

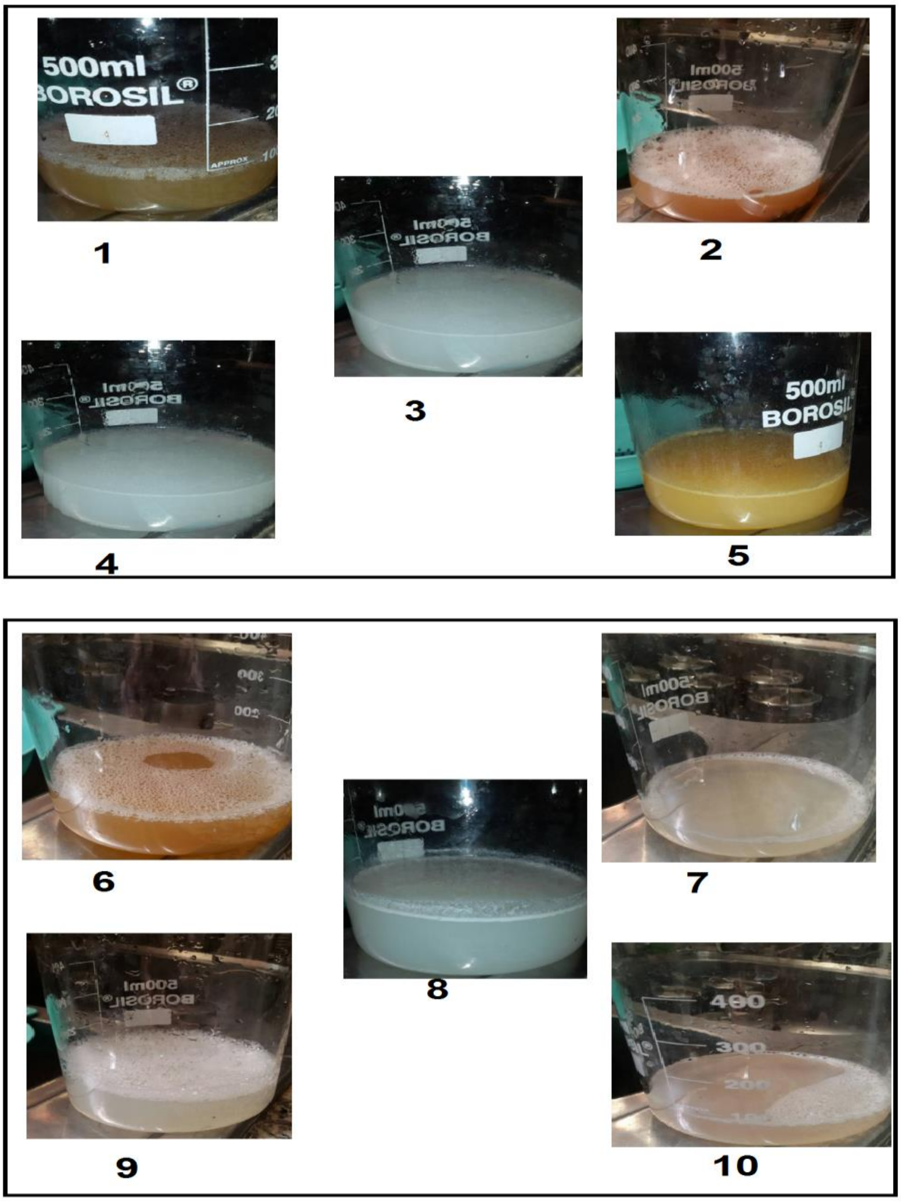


Figure 3: The wash fastness rating of cotton fabric dyed [CUM- Metal-phen]Complexes

Figure 4: Fastness level rubbing fastness ratings and chanced color

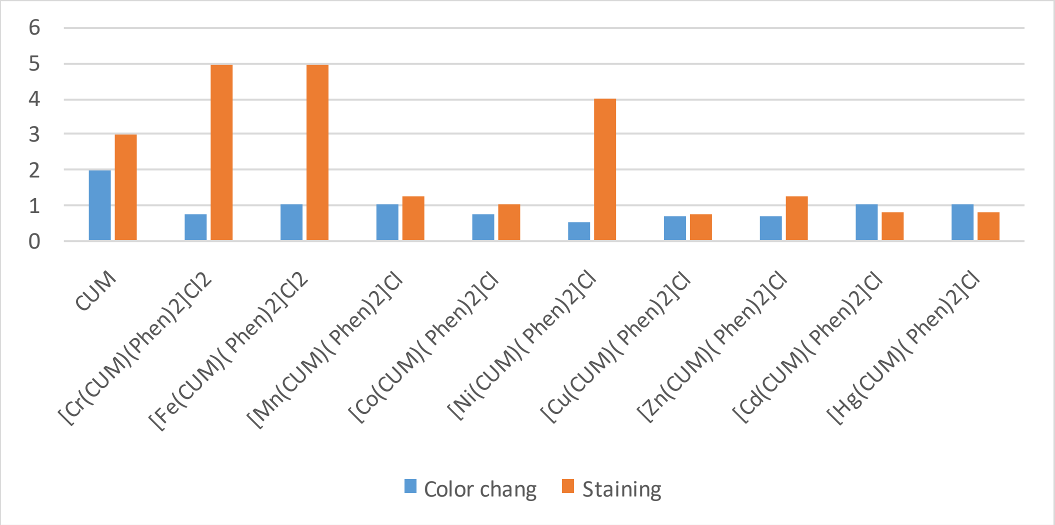
The good fastness of colour presented by Marigold flower dye with the utilization of various dyeing auxiliaries may be attributed to the two hydroxyl groups (Jothi, 2008).Using iron and copper sulphate on the samples dyed with Marigold flower extract as a mordant produced good light fastness. As discussed earlier by Jothi (2008), this may be due to the development of a complex with transition metal which is responsible for protecting the chromophores from photolytic degradation and due to the sorption of photons by chromophoric group which scatter their energy by resonating within the six member ring, thereby providing UV protection to the dye

The fastness properties have improved significantly, when different types of complexes. It is observed that the light fastness rating of (CUM) dye is lower than most complexes in this study and direct dyes have good fastness properties, It is because of the chromophore group structure of the (CUM) dye. Properties porous structure and capillaries in fully developed cotton should have free flow of liquor during dyeing. The wash fastness rating of cotton fabric dyed with acid is presented in table (5)

Table 5: Fastness properties of cotton fabric dyed with curcumin dye and [CUM- Metal- Phen] complexes

	Comp.	Color change	staining
1	CUM	2	3
2	[Cr(CUM)(Phen)$_2$]Cl$_2$	3/4	5
3	[Fe(CUM)(Phen)$_2$]Cl$_2$	1	5
4	[Mn(CUM)(Phen)$_2$]Cl	1	5/4
5	[Co(CUM)(Phen)$_2$]Cl	3/4	1
6	[Ni(CUM)(Phen)$_2$]Cl	1/2	4
7	[Cu(CUM)(Phen)$_2$]Cl	2/3	3/4
8	[Zn(CUM)(Phen)$_2$]Cl	2/3	5/4
9	[Cd(CUM)(Phen)$_2$]Cl	1	4/5
10	[Hg(CUM)(Phen)$_2$]Cl	1	4/5
Wash fastness	5- very good ,4-4/5 good ,1/ 2-1 ,2/3-2 poor		

It is observed that the light fastness rating of cucumin dye is lower than wash and rubbing fastness ratings in cotton fabric. **Scheme (3)** It is because of the chromophore group structure of the (phen) and(CUM) dye. Samples were analyzed for wash fastness (ISO 105- C10:2006) in terms of change in shade as well as staining on the adjacent white fabric by Grey-Scale.



Scheme (3): Cumulative color fastness of cotton fabric samples dyed with curcumin dye and [CUM- Metal- Phen] complexes

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