

## Spectral and antibacterial investigations of Er(III) Juglonates

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**Abstract :** Lawsone, Juglone, Phthiocol, Plumbagin and their Metal chelates of Er(III) are prepared. The chemical composition of Ligand and chelates are obtained by microanalysis and thermogravimetric analysis. The spectroscopic investigations are done with the help of IR spectroscopy and UV-visible spectroscopy. The morphological changes of chelates are studied from SEM photographs. The antibacterial activity of ligands and their metal chelates is examined against four bacterial strains; Bacillus subtilis, Staphylococcus aureus, Escherichia coli, Pseudomonas aeruginosa. The spectral, thermal and antibacterial properties are studied with special reference to ring isomerism within the isomeric pairs of chelates.

**Keywords :** Er(III) chelates, Juglones, spectroscopic properties, antibacterial activity.

### Introduction

The 'Juglons' which are hydroxyl derivative of 1,4 naphthoquinones is a typical class of ligands. All Juglons are strong chelating agents and are versatile in nature exhibiting attractive biological, analytical, pharmacological properties. Therefore these ligands are studied by various researchers from last fifty years.

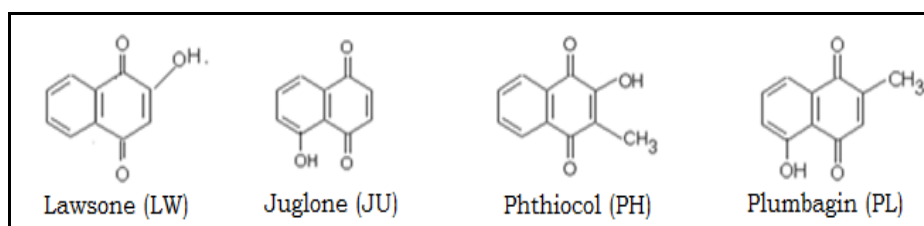


Fig-1 Parent members of juglone

The parent members of Juglone series are shown in Fig-1. (I) Lawsone, (II) Juglone, (III) Phthiocol, (IV) Plumbagin are selected for the present study and their isomeric chelates with Er(III) are prepared and studied. Lanthanide chelates are found to be useful and exhibiting applications in the fields like fluorescence [1], antimicrobial [2] and anticancer agents [3], planar waveguide amplifiers [4]. Spectral, structural and antimicrobial properties of some Sm(III) and Tb(III) juglonates are reported previously [5-7]. Due to the change in position of -OH group on naphthoquinone moiety the Lawsone and Phthiocol are position isomers of Juglone and Plumbagin respectively. As a result of chelation with metal ion, Lawsone and Phthiocol form five membered ring while the Juglone and Plumbagin form six membered ring. Due to change in ring size they are recognized

as ring isomers of each other. Therefore the comparative study of spectral, thermal and antibacterial properties in ring isomeric chelate of Er (III) is an attractive aspect of present study.

## Materials and Method

### Synthesis of ligands

The ligand Lawsone and Plumbagin were purchased from Aldrich and Hi media respectively. The Juglone and Phthiocol were prepared by using standard procedures as reported by Radt[8] and Fisher[9] respectively.

### Synthesis of Chelates

The methanolic solution of the ligand and aqueous solution of Lanthanide metal salt in distilled water are taken in the ratio 3:1 proportion and these ligand and salt solutions are mixed and refluxed for 45 min at 60°C. Then the pH of mixture is adjusted between 5 to 6 by 10 % aq. ammonia solution and then reaction mixture is stirred about 3 hours. After cooling the precipitate was kept in refrigerator overnight and the product was filtered and it was dried in vacuum desiccators.

### Instrumental techniques

Chemical characterization of ligands and their chelates is done by elemental analysis for the percentage of Carbon, Hydrogen and residue (as metal oxide) by using through Thermo Finnigan CHNS and O analyzer and thermal analysis was done on simultaneous thermal analyzer Shimadzu modelDTG-60. The morphological study is carried out with the help of photographs obtained from scanning electron microscope JEOL-3SM-5200. The infrared spectra are recorded on a Thermo Scientific (Nicolet) spectrophotometer in the region 4000-450  $\text{cm}^{-1}$  and solid state electronic spectra of the ligands and their Erbium chelates are recorded on U.V-300 double spectrophotometer in the region 200-1100 nm.

## Results and Discussion

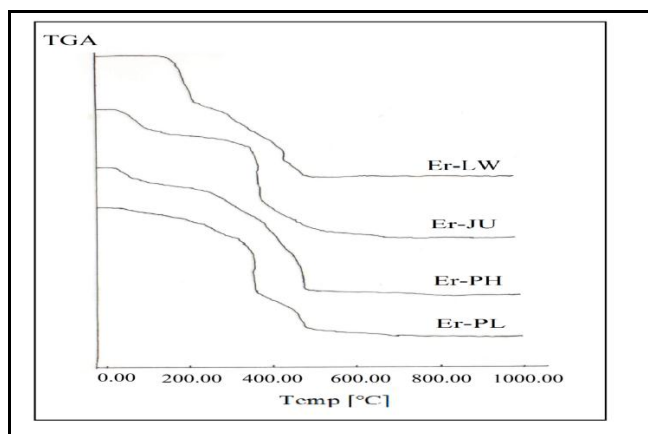
All the Er(III) chelates exhibit attractive colours in solid state. The Lawsonate possess deep orange colour, Juglonates show black colour and phthiocolate are brown in colour and Plumbaginate possess deep brown colour. The analytical data of the chelates, like elemental analysis, physical properties and molecular composition of chelate is presented in Table-1.

**Table.1: Analytical Data of Er(III) chelates**

Sr. No	Empirical Formula	Color	Yield(%)	Elemental Analysis: Found (Calcd.)		
				C	H	M(asMO)
1.	Er(LW) <sub>3</sub> 2H <sub>2</sub> O	Deep orange	68.74 %	49.63 %	3.03 %	23.02 %
	Er.C <sub>30</sub> H <sub>19</sub> O <sub>11</sub>			(49.10 %)	(2.92 %)	(23.31 %)
2.	Er(JU) <sub>3</sub> 2H <sub>2</sub> O	Black	66.07 %	49.63 %	3.03 %	23.02 %
	Er.C <sub>30</sub> H <sub>19</sub> O <sub>11</sub>			(48.86 %)	(2.96 %)	(22.66 %)
3.	Er(PH) <sub>3</sub> .2H <sub>2</sub> O	Brown	68.94 %	51.61 %	3.64 %	21.76 %
	Er.C <sub>33</sub> H <sub>25</sub> O <sub>11</sub>			(51.47 %)	(3.44 %)	(21.34 %)
4.	Er(PL) <sub>3</sub> .2H <sub>2</sub> O	Deep brown	66.38 %	51.61 %	3.64 %	21.76 %
	Er.C <sub>33</sub> H <sub>25</sub> O <sub>11</sub>			(51.18 %)	(3.27 %)	(21.61 %)

LW: Lawsone JU: Juglone PH: Phthiocol PL: Plumbagin M: Metal MO: Metal Oxide

### Thermal study



**Fig-2. Thermogram of Er(III) Juglonates**

The thermograms of Er(III) juglonates are shown in Fig-2. Thermograms of the isomeric pairs are distinctly different in nature. Careful study of the thermograms is useful to estimate the number of lattice and coordinate water molecules, decomposition of chelates and the percent residue left after complete decomposition[7,10]. The weight loss in thermal decomposition of the chelates takes place in three to four steps. In the first step loss of two lattice and coordinated water molecules[6] takes place along with partial decomposition of the ligand except Er(III) Plumbaginate. In Er(III) Plumbaginate only two water molecules are lost in first step. In the subsequent three steps partial decomposition of the remaining ligands takes place. The residue which remains at the end of analysis is tentatively matching with percent Erbium oxide. The final decomposition temperatures of Er(III) Juglonates and Plumbaninates are in range of 715-725 °C where as for Er(III) Lawsonates and Phthiocolates they are in the range of 545-570 °C.

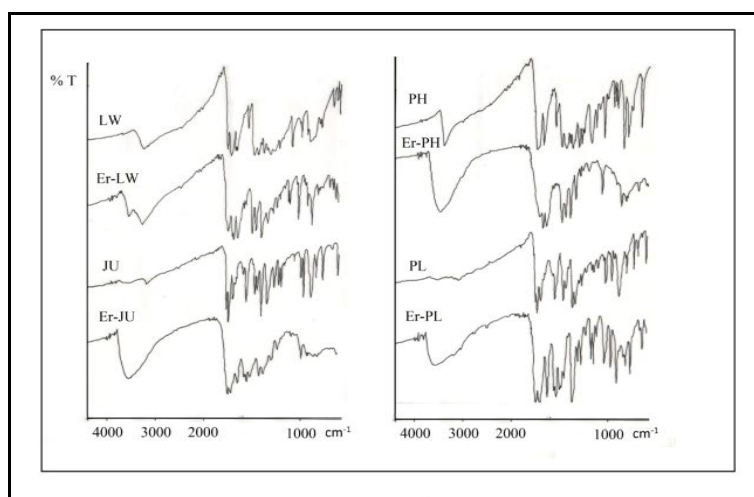
Therefore in general, Er(III) Juglonates and Plumbaninates are thermally more stable than Lawsonates and Phthiocolates. This observation indicates that six member ring chelates possess greater thermal stability than five member ring chelates.

### Infrared spectroscopy

The Infrared spectra of the ligands and their metal chelates are shown in Fig-3 and the significant Infrared peak values are summarized in Table-2.

**Table-2 Significant IR peaks of Ligands and their metal Chelates**

Sr. No	Compound	$\nu$ (OH) (cm <sup>-1</sup> )	$\nu$ (C=O) (cm <sup>-1</sup> )		$\nu$ (C-O) (cm <sup>-1</sup> )	-CH <sub>3</sub> (cm <sup>-1</sup> )
			Chelated	Free		
1)	LW	3170	1592	1678	1214	---
2)	Er-LW	3468	1542	1588	1223	---
3)	JU	---	1643	1664	1225	---
4)	Er-JU	3399	1594	1627	1246	---
5)	PH	3325	1590	1656	1208	2942
6)	Er-PH	3412	1555	1589	1230	2928
7)	PL	---	1644	1663	1230	2965
8)	Er-PL	3464	1602	1643	1254	2919



**Fig-3 Infra Red spectra of Ligands and their Metal Chelates**

#### **OH stretching frequency:**

The Lawson shows  $\text{-OH}$  stretching frequency at  $3170\text{cm}^{-1}$  which is absent in Juglone due to strong intramolecular hydrogen bonding. The Phthiocol shows  $\text{-OH}$  stretching frequency at  $3325\text{cm}^{-1}$  which is absent in Plumbagin due to intramolecular hydrogen bonding. After chelation this frequency, becomes broad and shifted to higher wave number ( $3468\text{cm}^{-1}$ ) in Er-LW, while in Er-JU a new broad is appeared at  $3399\text{cm}^{-1}$ . The  $\text{-OH}$  frequency at  $3325\text{cm}^{-1}$  in Phthiocol, becomes broad and is shifted to higher wave number ( $3412\text{cm}^{-1}$ ) in Er-PH as a result of chelation. In Er-PL a new broad peak is observed at  $3464\text{cm}^{-1}$ . In all four chelates, it is assignable to lattice or coordinated water [11].

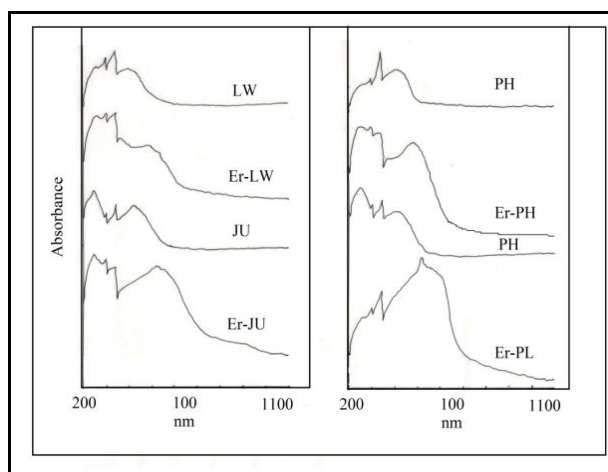
#### **C=O Stretching Frequency:**

In the spectra of ligands and their metal chelates, two nonequivalent  $\text{C=O}$  groups are present. The first  $\text{C=O}$  group is next to  $\text{OH}$  group it is called as 'chelated  $\text{C=O}$ ' and the other group is called 'free  $\text{C=O}$ ' [12,13]. The chelated  $\text{C=O}$  frequency of all the ligands is observed in the range of ( $1590\text{-}1644\text{cm}^{-1}$ ) and is shifted to lower wave numbers as a result of chelation. Due to the transfer of electron density to metal through 'chelated  $\text{C=O}$ ' this bond becomes weak. This indicates the oxygen from chelated  $\text{C=O}$  is the donor site. The free  $\text{C=O}$  frequency of ligands is observed at ( $1656\text{-}1678\text{cm}^{-1}$ ) and after chelation this frequency is also shifted to lower wave number, due to the involvement of this bond in chelation indirectly.

#### **C-O Stretching Frequency:**

This  $\text{C-O}$  frequency is directly involved in chelation. The  $\text{C-O}$  stretching frequency of ligands is seen at ( $1208\text{-}1230\text{cm}^{-1}$ ) and after chelation it is shifted to higher wave numbers in all the chelates. This observation indicates that  $\text{C-O}$  bond becomes stronger during chelation than Ligands. This could be due to transfer of electron density from free  $\text{C=O}$  bond to  $\text{C-O}$  bond as a result of chelate formation.

## Electronic Spectroscopy



**Fig-4 Electronic Spectra of Ligands**

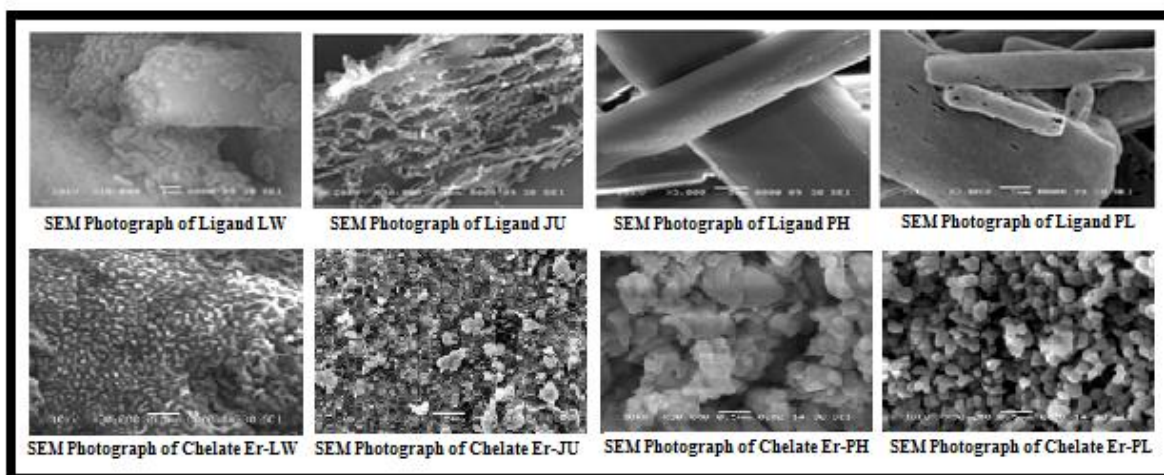
**Table 3:-Absorption maxima of electronic spectra their metal Chelates of Ligands and Their Chelates**

Sr. No	Compound	Principle band wavelength		
		BET $\lambda$ nm.	QET $\lambda$ nm.	$n-\pi^*/L \rightarrow M/$ f-f transition $\lambda$ (nm)
1)	LW	260	343	394
2)	Er-LW	260	342	493(86)
3)	JU	247	367	425
4)	Er-JU	248	342	528(103)
5)	PH	265	352	418
6)	Er-PH	251	333	486 (68)
7)	PL	248	363	407
8)	Er-PL	266	343	525(118)

The ligands as well as their metal chelates exhibit three principal bands in their electronic spectra. The first band is due to benzenoid electron transfer (BET), second is due to quinonide electron transfer (QET), and third is due to  $n \rightarrow \pi^*$  [14]. In general spectra of chelates resembles with spectra of the ligands. After chelation with metal the BET and QET bands are shifted either longer or shorter wavelengths (Table-3). Notable change in the position, intensity and shape is observed in the last i.e. third band of the all spectra of the metal chelates. A large shifting in position to higher wavelength for this band is seen. This third band becomes broader due to mixing of  $n \rightarrow \pi^*$  transitions, ligand to metal charge transfer and f-f transitions in lanthanide ion.

The six membered Er(III) Juglonate and Plumbagininate show greater shifting of third band (by 103-118 nm) than respective five membered Er(III) Lawsonate and Phthiocolate (by 68-86 nm) showing effect of 'ring isomerism'.

### Scanning Electron Microscopy of Ligands and their Er(III) Chelates



**Fig-5 SEM Photographs of Ligands and Er(III) Chelates**

The SEM photographs of ligands and their Er(III) chelates are indicative of significant change in morphology of ligands as result of chelation. The Lawsonate show big lumps covered by dusty particles,

While after chelation, Er(III) Lawsonate show micro particles as seen in the photograph. Its isomer Juglone shows thin layers placed one above the other. As a result of chelation Er(III) Juglonate show small dusty particles. The Phthiocol shows a big rod shaped particles which are changed to square shaped particles with merged boundaries in Er(III) Phthiocolate. The particles of Plumbagin have porous rod like structure which become granular shaped with clear define boundaries in Er(III) plumbaginate. The effect of ring isomerism is thus prominently seen on the morphology of the chelates.

#### Antibacterial Activity of Ligands And Chelates

The ligands Lawson, Juglone, Phthiocol and Plumbagin exhibit powerful antimicrobial activity [15-19]. Therefore effect of chelation and ring isomerism on the antibacterial activity is an interesting aspect for present investigation. Chelation with the metal ion alters the activity and it is either enhanced or decreased due to introduction of metal ion. Some transition metal Juglonates and some lanthanide Juglonates exhibit significant antimicrobial activity [20-22].

#### Materials and Method:

The salt  $\text{ErCl}_3 \cdot 6\text{H}_2\text{O}$ , selected ligands and their Er(III) chelates are subjected for the antibacterial activity study using standard well diffusion method as described in our previous work [5,7]. Four bacterial strains, *Escherichia coli* (NCIM – 2065), *Pseudomonas aeruginosa* (NCIM-2948) which are Gram negative bacteria and *Staphylococcus aureus* (NCIM – 2079) and *Bacillus subtilis* (NCIM – 2063) which are Gram positive bacteria are undertaken for the study. The strains were obtained from National collection of Industrial Microorganisms division of National Chemical Laboratory (NCL), Pune. The salt, ligands and the chelates are studied at three different concentrations, 1mg/ml, 1.5mg/ml and 2mg/ml by dissolving these compounds in DMSO.

The bacterial plates were incubated for 24hrs, at 37°C. After incubation the organisms which are sensitive are inhibited by the selected ligands and chelates due to which inhibition zones are developed. The diameters of these inhibition zones were measured in mm. The antimicrobial activity in the present work is expressed in terms of area of circular inhibition zone ( $\text{mm}^2$ ) calculated from  $\pi r^2$  (where  $r$  = radius i.e. 0.5 diameter). This modified method is more convenient for comparative purpose as suggested by Kulkarni [5]. The results at various concentrations are presented in Table-4. Most of the chelates show significant activity at concentration

1.5mg/ml. Therefore comparison of their activity is done at this concentration (Table-4).

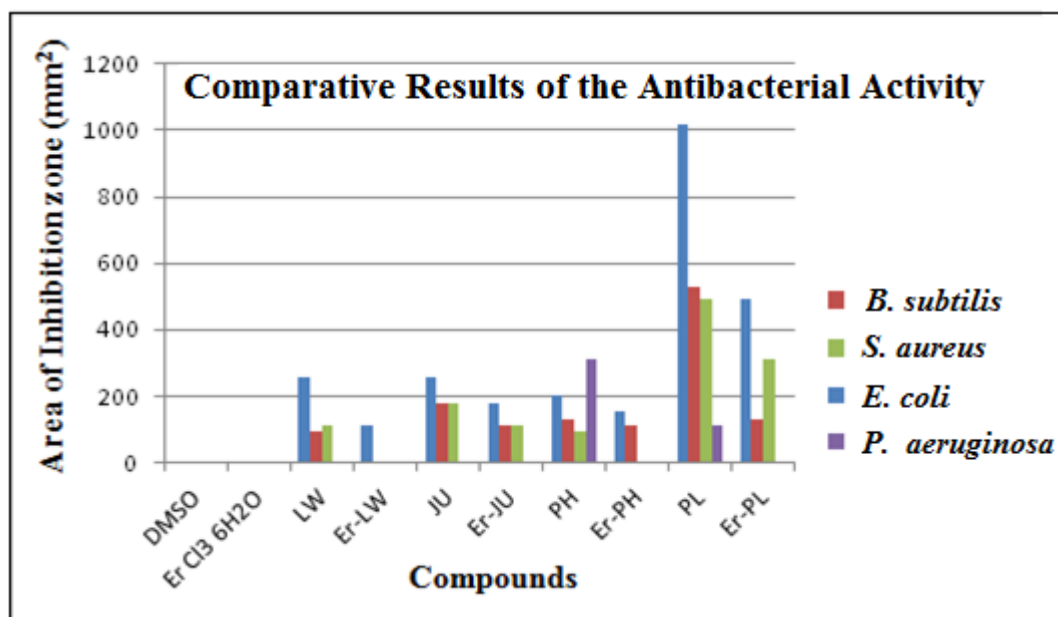
**Table-4 Antibacterial activity of Juglones and their Er(III) Juglonates with Different concentration**

Compo unds	Conc. Mg/ml.	<i>B. subtilis</i>		<i>S. aureus</i>		<i>E. coli</i>		<i>P. aeruginosa</i>	
		A	B	A	B	A	B	A	B
DMSO	---	----	----	----	----	----	----	----	----
Er Cl3.6 H2O	1.0/1.5/ 2.0	----	----	----	----	----	----	----	----
LW	1.0	10	78.5	10	78.5	13	132.66	----	----
	1.5	11	94.985	12	113.04	18	254.34	----	----
	2.0	15	176.62	16	200.96	18	254.34	----	----
Er-LW	1.0	---	---	---	---	11	94.985	----	----
	1.5	---	---	---	---	12	113.04	----	----
	2.0	---	---	11	94.985	13	132.66	----	----
JU	1.0	15	176.62	15	176.625	18	254.34	----	----
	1.5	15	176.62	15	176.625	18	254.34	----	----
	2.0	16	200.96	15	176.625	18	254.34	----	----
Er-JU	1.0	10	78.5	12	113.04	12	113.04	----	----
	1.5	12	113.04	12	113.04	15	176.625	----	----
	2.0	13	132.66	14	153.86	13	132.66	----	----
PH	1.0	13	132.66	10	78.5	14	153.86	----	----
	1.5	13	132.66	11	94.98	16	200.96	20	314.00
	2.0	14	153.86	11	94.98	16	200.96	12	113.04
Er-PH	1.0	---	---	---	---	12	113.04	----	----
	1.5	12	113.04	---	---	14	153.86	----	----
	2.0	---	---	---	---	13	132.66	----	----
PL	1.0	26	530.66	25	490.62	34	907.46	11	94.985
	1.5	26	530.66	25	490.62	36	1017.3	12	113.04
	2.0	27	572.26	25	490.62	36	1017.3	14	153.86
Er-PL	1.0	16	200.96	21	346.185	29	660.185	----	----
	1.5	13	132.66	20	314.00	25	490.625	----	----
	2.0	13	132.66	23	415.265	27	572.265	----	----

## Result and discussion of antibacterial activity

The ligand LW, JU, PH and PL exhibit significant activity against *E.Coli*, *B.Subtilis* and *S.aureus*. Among the four ligands Phthiocol and Plumbagin exhibit moderate activity against *P. aeruginosa* while Lawson and Juglone show no activity for the same. The ligand Plumbagin show highest antimicrobial activity against three selected bacteria except against *P. aeruginosa*. It is notable that activity of Phthiocol (314mm<sup>2</sup>) against *P. aeruginosa*, which is a multidrug resistant strain, is found to be greater than Plumbagin (113mm<sup>2</sup>) at concentration 1.5mg/ml.

Erbium chloride show zero activity against all four microorganisms. In general, the antibacterial activity of ligand is greater than their respective chelates. The area of inhibition zone against Gram negative bacteria (*E.Coli*,) is greater than gram positive bacteria (*B.Subtilis*, *S.aureus*). As shown in Fig-6. All Er(III) Juglonates show notable activity against *E-Coli*. Except Er(III) Lawsonate they show moderate activity against *B.Subtilis*. Against *S.aureus*, only Er(III) Juglone and Er(III) Plumbaginate show activity while activity of all four chelates is diminished against *P. aeruginosa*. Effect of ring size of chelates is clearly seen on the activity. The six membered ring chelates Er-JU and Er-PL show greater activity than five membered ring chelates Er-LW and Er-PH respectively against three microorganisms as depicted in Fig. no-6



**Fig-6 ( Bar Digram) Comparison of the Antibacterial Activity of Juglones and their Er(III) Juglonates at concentration 1.5mg/ml**

## Conclusion

Consequence of chelation with Er(III) and ring isomerism is studied on the selected ligands ie on Lawsons, Juglone, Phthiocol and Plumbagin. Their spectral and antibacterial properties are compared within isomeric pairs. The IR spectra of the isomeric chelates indicates that six member chelates of Er(III) possess stronger metal to ligand bonds as compare to five member chelates of Er(III). In electronic spectra large shifting (by 68-118 nm) of last band is observed as a result of chelation. This band becomes broad in nature due to mixing of bands, metal-ligand charge transfer bands, f-f transitions as well as  $n \rightarrow \pi^*$  transition bands in the chelates. The isomeric pairs of Er(III) Juglonates show significant difference in their morphology as observed from SEM photographs. The antibacterial activity of Er-Juglonate and Er-Plumbaginate, containing six member ring is found to be superior than Er-Lawsonate and Er-Phthiocolate, containing five member ring against all selected bacterial strains.

## Acknowledgements

Authors are thankful to Prof. Dr. S.S. Kadam, Vice Chancellor, Bharati Vidyapeeth Deemed University Pune, Principal Dr. K.D. Jadhav, Y.M. College Pune, for providing necessary facilities and constant encouragement. Authors are also thankful to Dr. B.A. Kulkarni and Dr. P.S. Khandagale for their valuable suggestions.

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