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Synthesis, Spectroscopic and Biocidal activities of Environmentally safe Agrochemicals.

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Abstract

The synthesized copper soaps and their urea and benzothiazole complexes have been confirmed by IR, NMR spectral analysis. The antifungal activities of copper soaps derived from mustard and sesame oils and their urea benzothiazole complexes have been evaluated by testing against *Aspergillus Fumigatusa* and *Aspergillus Niger* at different concentrations by P.D.A. technique. This work is useful in agricultural industries and various other fields.

Key words: Copper surfactants, Anti-fungal studies, IR, NMR, ESR, Edible oils.

Introduction

The synthesis and assaying of the biological potential of new agrochemicals have received considerable interest in the recent years. Agrochemical compounds are of great importance as they are used as natural insecticides, herbicides and fungicides in the field of agriculture and soil sciences. The nature of surface-active agents and colloids plays a vital role in determining the chemical and biological behaviour of these systems. The use of agrochemicals, i.e. surfactant as preservation of wood, protecting crops, water proofing and repelling, various industries of rubber, paints and varnishes etc. are the relatively newer applications (Sharma *et al.* 2017). Shidore**,** M. *et al.* studied Benzylpiperidine-Linked Diarylthiazoles as Potential Anti-Alzheimer's Agents and evaluate its biological activity (Shidore**,** M. *et al.* 2016). Arora P. *et al.* reported 2,4-disubstituted thiazoles as multitargated bioactive molecules. (Arora P. *et al.* 2016). Bakr F. *et al.* synthesize and evaluate biological activity of some new 1,2,3- triazole hydrazone derivatives. (Bakr F. *et al.* 2015).

The physicochemical and ultrasonic studies of these agrochemicals derived from different composition of long chain fatty acids with transition metal copper and their complexes with nitrogen and sulphur containing ligands which are biodegradable, may play a significant role in biological activities and have sufficient pharmaceutical, industrial and analytical application due to their surface-active properties (Sharma *et al.* 2017, Tank *et al.* 2017).

Putta**,** R.R. *et al.* synthesize Bis-heteroaryl Hydrazines and evaluate its anti-allergic Activity (Putta**,** R.R. *et al.* 2017). Nair *et al.* studied the biological studies of Co(II), Ni(II), Cu(II) and Zn(II) complexes involving a potentially tetradentate Schiff base ligand (Nair *et al.*). Electrochemical behaviour and thermal decomposition studies of some transition metal complexes with an azo derivative have been reported by (Sujamol *et al.* 2010). Reham Ezzat Shafek *et al.* studied phytochemical studies and biological activity of Dodonaea Viscosa flowers extract (Reham Ezzat Shafek *et al.* 2015).

Survey of literature shows that agrochemicals derived from the different composition of long chain fatty acid and their complexation with nitrogen and sulphur containing ligands i.e. urea and benzothiazole derivatives play a vital role in biological activities. Their thermal and photochemical degradation studies were reported by Sharma *et al.* (2013, 2015, 2017) in many papers.

These studies will generate new hopes to analyze the role of organo copper surfactants in enhancing the performance of the various biological activities and anticancer agent, ulcer inhibitor, anti- asthmatic, anti-inflammatory, anti -bacterial etc. In continuation of our previous work (Sharma et al 2012), in the present study, six new agrochemicals compounds derived from two edible oils (i.e. mustard and sesame) with different compositions of long chain fatty acid with transition metal copper and their complexes with nitrogen and sulphur containing ligands were synthesized.

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Materials and Methods

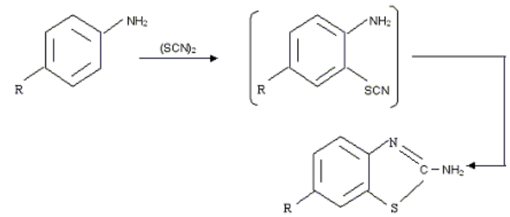
Synthesis of Agrochemicals

All the chemicals used were of LR/AR grade. Before synthesis of agrochemicals solvents was purified by standard procedure. Oils were procured directly from the seeds of mustard and sesame. Synthesis of these new agrochemicals with transition metal copper was done by refluxing the two edible oils with 2N KOH solution and alcohol for about 3hr. (direct metathesis). The excess of KOH was neutralized using 1N HCL. Saturated solution of copper sulphate was then added to it for conversion of neutralized soap into copper soap (new agrochemicals) [Tank *et al.* 2017]

The synthesized agrochemicals so obtained were filtered washed with warm water followed by alcohol dried at 50^{0}C and recrystallized with hot benzene. The fatty acid composition of these edible oils were confirmed through GLC of their methyl esters and is given in (Table 1)

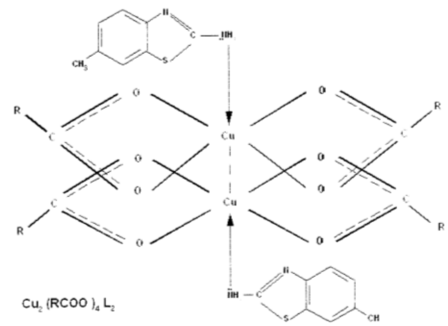
Table – 1 Fatty acid composition of oils used for copper agrochemicals synthesis

Name of Oil	% Fatty Acid					
	16:0	18:0	18:1	18:2	18:3	other acids (C_{20}-C_{22})
Mustard Oil	2	1	25	18	10	41
Sesame Oil	8	4	45	41	-	-



Where R- methyl group

Structure of copper sesame benzothiazole complex



L = 2-amino-6methyl benzothiazole
R = fatty acid composition of oils given in (Table-I)

Table – 2 Analytical and physical data of copper agrochemicals and their urea and benzothiazole complex derived from mustard and sesame oil

S.No.	Name of Agrochemicals	Colour	Melting Point (^{0}C)	Yield (%)	Metal Content (%) Observed	Calculated	S.V.	S.E.	Average Molecular Weight
1	CM	Green	90	80	9.58	9.11	175.80	319.10	699.72
2	CSe	Green	100	85	10.05	9.72	188.70	297.29	656.08
3	CMU	Dark Green	72	85	8.46	8.35	-	-	759.72
4	CSeU	Dark Green	90	86	-	-	-	-	705.78
5	CMB	Dark Green	95	91	7.11	7.18	-	-	884.224
6	CSeB	Dark Green	90	86	9.16	8.98	-	-	821.66

Synthesis of Ligand (Benzothiazole)

Benzothiazole is derivative of anilines and play a significant role in biological activities and have sufficient industrial and analytical applications. Benzothiazole possesses nitrogen and sulphur atoms which are responsible for their pharmacological activities.

The ligand 2-amino 6- methyl benzothiazole was synthesized using thiocyanation method. Ligand 2-amino benzothiazole are prepared by thiocynation of para substituted arylamines, in the presence of thiocyanogen gas, which is generated in situation by the reaction of cupric chloride and sodium thiocynate or bromine and potassium thiocyanate (Khan *et al.* 2017)

The purified agrochemicals synthesized from two edible oils was refluxed with ligand urea/ 2-amino-6methyl benzothiazole in 1:1 ratio using benzene as a solvent for 1½ hr. It was then filtered hot dried, recrystallized and purified in hot benzene; TLC using silica gel was used to check the purity of the complex.

In general, all the six new agrochemicals are soluble in benzene and other organic solvents but insoluble in water. The entire synthesized compounds are stable at room temperature.

The new synthesized agrochemicals are abbreviated as follows:

1. Copper Mustard Agrochemical CM
2. Copper Sesame Agrochemical CSe
3. Copper Mustard Urea Complex CMU
4. Copper Mustard Benzothiazole Complex CMB
5. Copper Sesame Urea Complex CSeU
6. Copper Sesame Benzothiazole Complex CSeB

Their physical parameters like saponification value (S.V.) saponification equivalent (S.E.), average molecular weight are given in (Table 2).

By elemental analysis 1:1 (Metal: Ligand) type of stoichiometry has been suggested for these agrochemicals.

Table – 3 Infra Red Spectral Data for Copper (II) Mustard / Sesame Agrochemicals and their Complexes

Absorption Bands	CM (cm^{-1})	CSe (cm^{-1})	CMU (cm^{-1})	CSeU (cm^{-1})	CMB (cm^{-1})	CSeB (cm^{-1})
Absorption Olefinic = C-H Stretching	3010	3010	3010	3010	3010	3010
CH_3 and CH_2, C-H Anti Sym Stretching	2930.7	2930.7	3010	3010	3010	3010
CH_3 and CH_2, C-H Sym, Stretching >C=O Stretching	1708	2930.7	3010	3010	3010	3010
COO^-, C-O Anti-Sym Stretching	1591.5	1591.5	3010	3010	3010	3010
COO^-, C-O Anti-Sym Stretching	1375	1375	3010	3010	3010	3010
CH_3, C-H Bending (Twisting and Wagging)	1305	1375	3010	3010	3010	1305
CH_3, C-H Rocking	1150	1150	3010	3010		
CH_2, C-H Rocking	731	731	3010	3010		
Cu-0 Stretching	424	731	3010	3010		
NH_2, N-H Stretching	-	-	3350 – 3500	3010	3300	3300
C-N Stretching	-	-	1418.4	1418.4	1443	1445
C-N Stretching	-	-	-	-	1320	1320

For calculation of biological activity, the glassware were thoroughly washed and cleaned with chromic acid, followed by washing with distilled water. Now, they were sterilized by keeping them in hot air oven at 160 ^{0}C for 24 h. All operations concerning inoculation are done in a completely sterilized chamber. The inoculation chamber was fitted with ultra-violet (UV) tube. For preparation of agar slant, a required number of culture tubes are taken and about 12 ml to 15 ml of agrochemical in liquefied agar medium is poured in each of them. The tubes are now cotton plugged and sterilized in an auto clave after the sterilization is over the tubes was taken out. The culture medium used for the growth of the organism in the present study was natural media i.e. P.D.A. (Potato dextrose agar). The test organisms used in the present study were *Aspergillus Niger* and *Aspergillus Fumigatus*. These organisms were isolated from their natural habitat and their purified, characterized and identified. Inoculums / broth were prepared by serial dilution method.

Spectral Analysis

To study the structure of these agrochemicals the infra-red (IR) absorption spectra of compounds were obtained on a Perkin Elmer 5100, 4367 (200cm^{-1}) (4000-200cm^{-1}) from RSIC (Regional Sophisticated Instrumentation Centre) IIT (Indian Institute of Technology) Powai, Mumbai. India HNMR spectra were recorded at central salt and marine chemicals research institute (CSMCRI) Bhavnagar, Gujarat India using ($CHCD_3$) deuterated chloroform as reference.

IR Spectral Analysis

To study the structure of these agrochemical the IR spectra are recorded in (Table - 3).

The detailed infrared absorption spectral studies reveal that there is a marked difference between the spectra of oils and that of corresponding agrochemicals. In the spectra of edible oils (Fig. 1, 2) three distinct bands appear at 3008, 2930.7 and 2849.2cm^{-1} are due to = C-H stretching, C-H anti-sym. stretching, C-H sym. stretching vibration respectively. The strong absorption band at 1591cm^{-1} and another weak band at 1375cm^{-1} are due to carboxylate coo$^-$, c-o anti symmetric and symmetric respectively. Also >c=o stretching bands were observed at 1708cm^{-1}. The small peak corresponding to $–CH_2$ twisting and wagging has been observed at 1305cm^{-1}. Also peaks corresponding to $–CH_3$ and $–CH_2$ rocking have been seen at 1150cm^{-1} and 731cm^{-1} respectively. Copper-oxygen (Cu-O) stretching bands have been distinguished at 424 cm^{-1}.

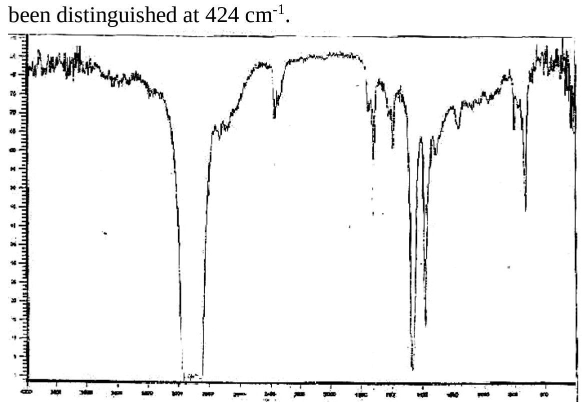


Fig.1 IR Spectra of Copper Mustard Soap

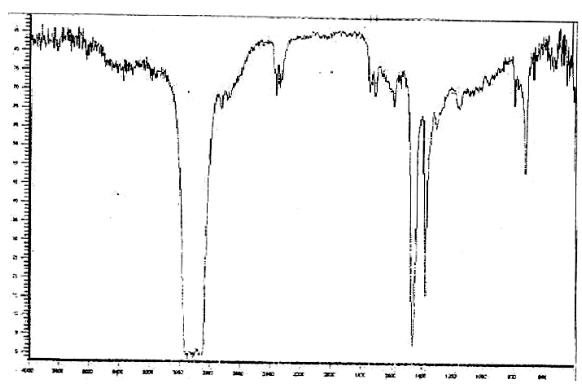


Fig.2 IR Spectra of Copper Sesame Soap

Apart from these absorption bands the following bands were also observed corresponding to ligand moiety. The C-N stretching band of primary amide was observed at nearly 1400 cm^{-1} i.e. 1418 cm^{-1} the absorption band 1708 cm^{-1} was found to be representative of amide >C=O group. A broad band near 3350 – 3500cm^{-1} was observed corresponding to N-H stretching of amides. C-N stretching (aryl tertiary) peaks are observed in the region 1360-1310 cm^{-1}. The spectrum also

Table – 4 NMR Spectral Data for Copper (II) Mustard / Sesame Agrochemicals and their Complexes

Peak / Signal	CM (δ)	CSe (δ)	CMU (δ)	CSeU (δ)	CMB (δ)	CSeB (δ)
$-CH_3-CH_2-R$	0.91	0.97	0.93	0.94	0.937	0.94
$-CH_2-CH_2-R$	1.28	1.293	1.29	1.290	1.295	1.295
-CH2-C=C	2.10	2.062	2.10	2.10	2.113	2.110
-C=C-H Vinylic Proton	5.49	5.47	5.50	5.50	5.504	5.502
$-C=C-CH_2-C=C-$	2.86	2.87	2.87	2.87	2.872	2.871
-NH2 Broadened Peak	-	-	3.2-4.2	3.2-4.2	3.2-4.2	3.2-4.7
C-N Stretching	-	-	-	-	1320	1320

contains a broad at 3300cm^{-1} attributed to N-H stretching. The spectrum also shows a clear peak at 1095cm^{-1} which is due to Ar-Cl-Cl vibrations (Fig. 3)

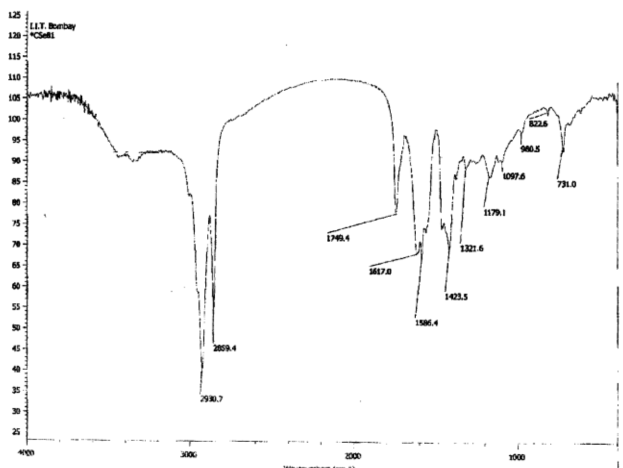


Fig. 3 IR Spectra of Cu (II) sesame benzothiazole

Thus by above observations it can be safely assumed that complexation of copper agrochemicals has taken place with ligand urea and benzothiazole respectively [Gunstone 1958]

NMR Spectral Analysis

NMR spectra of these agrochemicals are recorded in (Table-4). A Perusal of the spectra of copper agrochemicals and their complexes shows signal of aliphatic – CH_3 proton attached to $-CH_2$-R group at nearly δ-0.879 – CH_2 protons attached to CH_2-R group shows signal at δ-1.28. Other signal observed are corresponding to $-CH_2$ attached to one –C=C- at 2.10, while $-CH_2$ attached to two –C=C is observed at δ-2.86. Vinylic proton gives signal at δ-5.287. All the above peaks are due to long chain fatty acid content (R-) of the soap molecule [(R-COO)2Cu]. The broadened peak is observed at δ-4.142, δ-4.285 and δ-4.315 corresponding to $-NH_2$ proton. This peak indicates the coordination through the $-NH_2$ group of urea / benzothiazole segment to the metal atom of the soap segment. (Fig. 4) [Riddiek 1970]

Biocidal activity

Now a day's scientist developed a metabolic and antagonist theory of drug action. This filed led to the synthesis of many coordination compounds, which has been used for antibacterial and anti - tubercular activities. Agrochemicals synthesized from different containing ligands which are biodegradable may play a composition of long chain fatty acid with transition metal copper and their complexes with nitrogen and sulphur

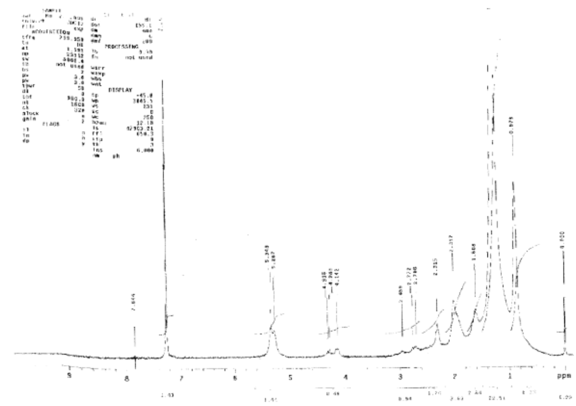


Fig. 4 NMR Spectra of Cu (II) sesame benzothiazole

significant role in biocidal activity [Mathur *et al.* 2011]. Aspergillus fumigatus is a ubiquitous saprophytic mold that forms airborne spores (conidia). In immune compromised hosts, A. fumigatus represents a major cause of morbidity and mortality. Aspergillus Niger causes a disease called black mould on certain fruits and vegetables such as grapes, apricots, onions, and peanuts, and is a common contaminant of food. A number of brands of different compounds containing nitrogen and sulphur are extensively employed as fungicide for the most important being as an agricultural fungicide and is extensively employed in formulated from as dust and wet table powders and pastes [Rai at el 2013]. A good fungicide should be toxic to the parasite and not to the host. It should be reasonably easy to prepare and not too expensive it should be capable of even distribution from the spraying or dusting machines [Fugui *et al.* 2013].Many fungicides known as insoluble copper have been placed on the market as substitutes for Bordeaux mixture [Choudhary *et al.* 2011]

All the above studies suggest that agrochemical derived from long chain fatty acid with transition metal copper and their complexes with benzothiazole and urea play a significant role in biocidal activities. The biocidal activities of this newly synthesized agrochemical have been evaluated by testing against various fungi *Aspergillus Niger* and *Aspergillus Fumigates* at different concentration by agar plat technique and serial dilution method [Sharma *et al.* 2008].The antifungal activity of the synthesized copper mustard, copper sesame agrochemicals and their complexes with urea and benzothiazole have been evaluated by testing against

Aspergillus Niger and *Aspergillus fumigates* by P.D.A. technique [Sharma *et al.* 2009]. The data were analyzed according to the following formula:

$$\% \, Inhibition = C - \frac{T}{C} * 100$$

Where C = number of fungal colonies (control plates after 72 h)
T = number of fungal colonies (test plates after 72 h) All the tests were performed in triplicate the standard deviation has been measured by the conventional measure of repeatability and the average was taken as final reading (Table -5) The results of ANOVA for the antifungal activities for all sops complexes are shown in Table 6. The predicted R^2 are in reasonable agreement and closer to1.0. This confirms that the experimental data are well satisfactory.

Results and Discussion

The Biocide and its activity against the species by copper sesame and mustard agrochemicals and their complexes with urea and benzothiazole ligands have been evaluated by testing against various fungi i.e. *Aspergillus niger, Aspergillus Fumigatus* at different concentrations by P.D.A. technique. The results of the biocidal screening data are recorded in Fig. 5-8

A perusal of results reveals that benzothiazole and urea complexes of copper and mustard agrochemicals show higher activity than pure agrochemicals. (Fig. 9)

Suggesting that complexes are more powerful antifungal agents. From the results it is apparent that the pure copper agrochemicals and their complexes with urea and benzothiazole have significant fungi toxicity at 10^4 ppm but their toxicity decreases markedly on dilution (at 10^3 ppm). Their comparative order could be as follow:

$10^4 > 10^3 > 10^2$ ppm.

It is evident that their efficiency increases with increases in concentration. Thus concentration plays a vital role in increasing the degree of inhibition. Also, on increasing the amount of solution in Petri plates from 1ml to 4 ml the % inhibition increases, suggesting that the % inhibition is affected by the increase in the concentration of the active fungicidal moiety in the analyzed system.

By earlier workers observations it was observed that enhanced activity of complexes might be due to synergistic mechanism i.e. the pure agrochemicals are less active but on complexation they show more activity in combination with ligands containing N and S atoms (Sharma *et al..* 2012, Tank *et al..* 2017)

The evaluation of antifungal studies further revealed that fungi toxicity of pure agrochemicals and their complexes also depends on the nature of the metal ions. From the results it shows that CM agrochemical is least fungi toxic (% inhibition lowest) in comparison to CSe agrochemicals the Biocide and it's activities against the species by copper sesame and mustard agrochemical is found in the order:

CSe> CM

And for complexes of agrochemicals the order of toxicity is as follow:

CseB>CSeU
CMB > CMU

The observation suggests that the agrochemicals possessing maximum biocidal activity have lowest molecular weight. Some recent studies about ant microbiological activities of early synthesized complex possessing thiazole or imidazole moieties also support our studies.

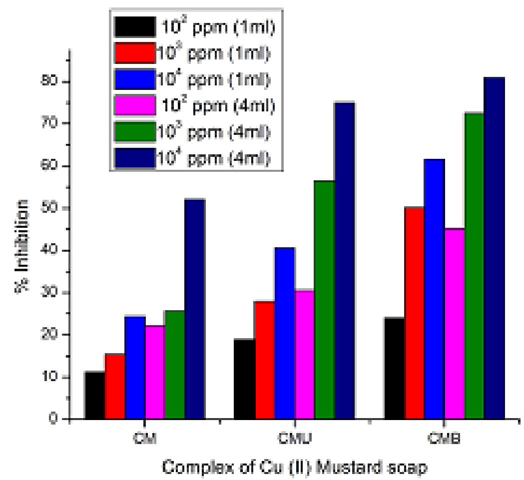


Fig.5 **Antifungal activity of copper mustard agrochemical (CM), their urea (CMU) & benzothiazole (CMB) complexes for fungi *Aspergillus Niger***

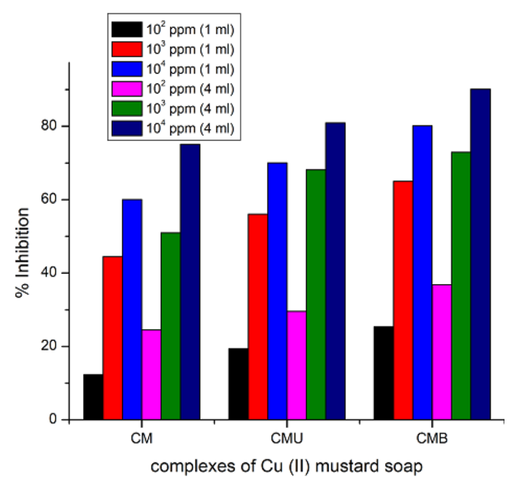


Fig.6 **Antifungal activity of copper mustard agrochemical (CM), their urea (CMU) & benzothiazole (CMB) complexes for fungi *Aspergillus Fumigatus***

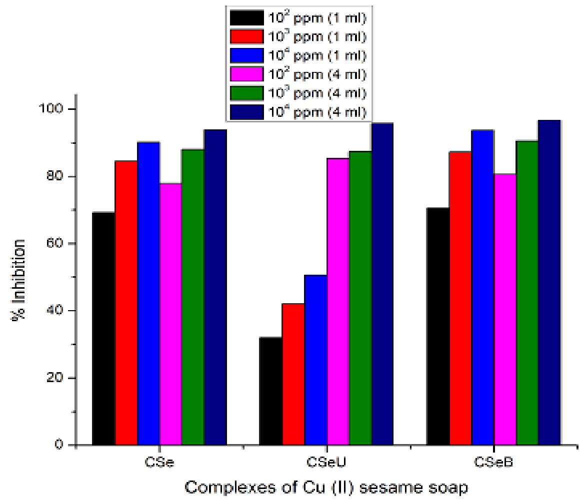


Fig.7 **Antifungal activity of copper sesame agrochemical (CSe), their urea (CSeU) &benzothiazole (CSeB) complexes for fungi *Aspergillus Niger***

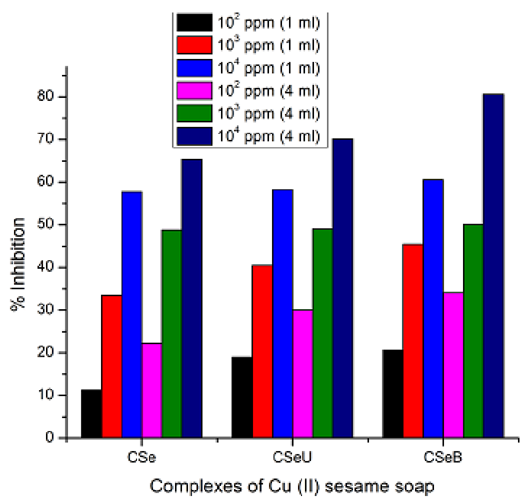


Fig.8 **Antifungal activity of copper sesame agrochemical (CSe), their urea CSeU) &benzothiazole (CSeB) complexes for fungi *Aspergillus Fumigates***

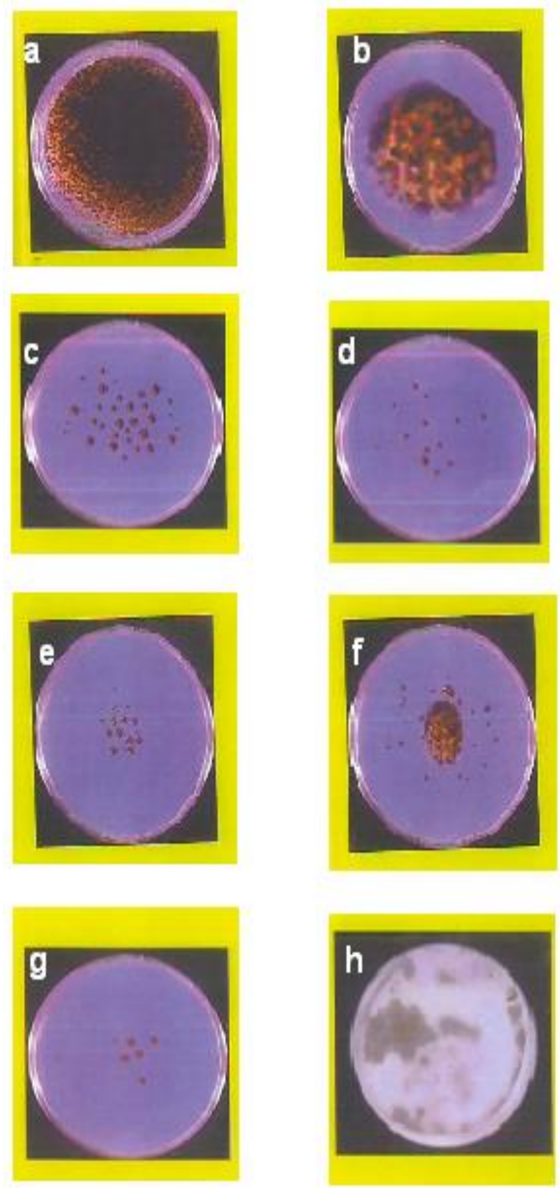


Fig 9 Antifungal effect of CSe soap and CSeB on *Aspergillus Niger a) Blank, b)* CSe, (10^2). c) CSeB, (10^2), d) CSe (10^3), e) CSeB (10^3), f) CSe (10^4), g) CSeB (10^4), h) Pure solvent benzene

Table- 5 Descriptive statics results for antifungal activities of Cu (II) soaps and its complexes

Fungi	*complex*	*Groups (ppm)*	*Subgroups (ml)*	*Count*	*Average % Inhibition*	*Std Error*	*Fungi*	*Average % Inhibition*	*Std Error*
Aspergillus Niger fungi	CSe	10^2	1	3	64.43	0.07	***Aspergillus Fumigates Fungi***	11.40	0.10
			4	3	73.40	0.10		22.30	0.42
		10^3	1	3	82.50	0.20		33.37	0.30
			4	3	84.63	0.13		48.30	0.42
		10^4	1	3	90.43	0.12		57.97	0.12
			4	3	94.53	0.15		65.73	0.27
	CSeU	10^2	1	3	32.00	0.25		19.20	0.17
			4	3	85.53	0.18		30.63	0.30
		10^3	1	3	42.27	0.29		41.30	0.26
			4	3	87.30	0.31		49.50	0.17
		10^4	1	3	50.37	0.30		58.80	0.31
			4	3	95.40	0.45		70.77	0.30
	CSeB	10^2	1	3	70.70	0.15		21.07	0.30
			4	3	80.77	0.30		34.00	0.36
		10^3	1	3	87.57	0.18		45.37	0.12
			4	3	90.87	0.18		50.73	0.33
		10^4	1	3	93.57	0.12		60.64	0.29
			4	3	96.00	0.40		80.87	0.20
	CM	10^2	1	3	11.67	0.12		12.62	0.25
			4	3	22.47	0.20		24.73	0.27
		10^3	1	3	15.37	0.26		44.60	0.26
			4	3	25.60	0.21		51.20	0.17
		10^4	1	3	24.57	0.18		60.60	0.32
			4	3	52.17	0.15		75.43	0.23
	CMU	10^2	1	3	18.37	0.09		19.38	0.09
			4	3	30.47	0.03		29.73	0.07
		10^3	1	3	27.43	0.29		56.63	0.22
			4	3	56.53	0.20		68.52	0.20
		10^4	1	3	40.53	0.20		70.87	0.20
			4	3	75.30	0.10		81.00	0.10
	CMB	10^2	1	3	24.48	0.21		25.87	0.20
			4	3	45.80	0.32		36.73	0.12
		10^3	1	3	50.50	0.21		65.43	0.23
			4	3	72.40	0.10		73.18	0.16
		10^4	1	3	61.53	0.20		80.60	0.15
			4	3	80.53	0.20		90.53	0.20

Table- 6 ANOVA results for antifungal activities of Cu (II) soaps and its complexes

Fungi	*Name of complex*	*SS*	*df*	*MS*	*F*	*P-value*	F_{crit}	*R- SQUARE*
Aspergillus Niger	CSe	1852	5	370	6872	2.7E-20	3.11	0.995
	CSeU	10985	5	2197	7800	1.2E-20	3.11	0.992
	CSeB	1329	5	266	1514	2.3E-16	3.11	0.996
	CM	3045	5	609	5565	9.4E-20	3.11	0.997
	CMU	6672	5	1334	14383	3.2E-22	3.11	0.991
	CMB	6087	5	1217	8619	6.8E-21	3.11	0.992
Aspergillus Fumigates	CSe	6687	5	1337	5015	1.8E-19	3.11	0.992
	CSeU	5281	5	1056	5296	1.3E-19	3.11	0.996
	CSeB	6516	5	1303	5593	9.1E-20	3.11	0.997
	CM	8002	5	1600	8155	9.5E-21	3.11	0.991
	CMU	9053	5	1811	24052	1.4E-23	3.11	0.992
	CMB	9723	5	1945	19312	5.4E-23	3.11	0.995

The data clearly indicates the inhibition power of agrochemical has been increased on complexation. All these studies will play a significant role in selection and promoters of ecofriendly and biodegradable fungicides, pesticides and insecticides.

Conclusion

Owing to proven industrial utility of copper mustard and copper sesame agrochemicals and their complexes with urea and benzothiazole in non- polar solvents have gained considerable popularity, due to their immense use and widespread applications such as wood preservation, foaming, wetting, biocidal, emulsification and lubrication etc.

The above applications stimulated our interest to extend synthetic investigations of ligands. Complexes of this ligand with transition metal surfactant are very important in various fields. In the present work synthesis of copper sesame and mustard agrochemical have been done. Complexation of these agrochemicals with nitrogen and sulphur containing ligand has been done which have remarkable chromogenic properties.

The present work deal with the synthesis spectral studies and biocidal activity of these agrochemicals. All the above studies led to the conclusion that copper mustard and sesame agrochemicals and their complexes due to its toxic and its bio degradable nature having fungicidal, herbicidal and many other biological activities. All these activity will play a significant role in their application in various fields of industries, pharmaceuticals, pesticides, wood preservation etc.

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