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Pesticidal activities of benzoin thiosemicarbazone and its complexes with Co(II) and Ni(II)

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Abstract

The schiff base benzoin thiosemicarbazone (BTSC) and two of its complexes with nickel [Ni(BTSC)$_2$] and cobalt [Co(BTSC)$_2$] were used to study their pesticidal activities against *Tribolium castaneum*. Probit mortality was studied by surface film treatment method at different doses of the compounds. The results showed that the LD_{50} values as recorded after 24 hours of treatment were 3.343363, 1.633098 and 3.344224 mg/cm^2 for BTSC, Co(BTSC)$_2$ and Ni(BTSC)$_2$, respectively as compared with 2.974 µg/cm^2 for a standard pesticide *malathion*. Better results were obtained when recorded with longer treatment time. These three compounds may, therefore, be considered as potent pesticides.

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Introduction

Pesticides are an integral part of modern agricultural production. From the early period of human civilization, it was realized that pests harm crops and transmit diseases both to human and animals. Since then various chemicals are being used as pesticides to kill pests. According to (Hill EG, 1978) more losses may occur in tropical countries through insect attack after harvest. In spite of our best efforts, world crop loss due to pests is approximately 35% of the total production each year **(**Pimental D, 1978).

This reduction in food grain production is further increased by the post-harvest losses caused by the insects and other pests **(**Wright JW, 1976). More than 2000 species of field and storage pests are engaged in such destruction causing enormous loss specially in developing Asian countries(Ahmed *et al.*,1986).

So the conservation of food from insect damage is of primary importance not only from the point of view of economic losses but for also of health reasons. The control process of insect by the application of chemicals has been known since early days.

The increasing serious problems of pest resistance to pesticides and contamination of the biosphere associated with the large scale use of broad spectrum synthetic pesticides have dictated the need for effective biodegradable, less hazardous, safe pesticides with greater selectivity. So the awareness has created a worldwide interest to look for the list of new suitable insecticides, which could be used only to destroy target insects leaving no harm to other components of the environment.

It is obviously a difficult task. One way is to overcome the problem is to find out new compounds having insecticidal activity with least toxicity. It is to be noted that schiff bases as well as the metal complexes have already been parallelly used (Ali *et al.*,2007) as insecticides. In this connection the synthesized schiff base BTSC and complexes of BTSC with Co(II) and Ni(II) have been studied here to find their capability as insecticidal agents against *Triboliumcastaneum*.

Materials and methods

Chemicals

All the chemicals used throughout the research work were purchased from BDH (England) and used without further purification. Solvents were distilled prior use.

General procedure for the synthesis of the compounds

The compounds were synthesized according to the method as described in the literature(Chinnasamy *et al.*, 2010; El-Shahawi *et al.*, 2013; Pande *et al.*, 2011). For benzoin thiosemicarbazone (BTSC), benzoin and thiosemicarbazide (1:1 molar ratio) were mixed together and refluxed for a period of 3-4 hours and then distilled to half of the total volume. A saturated solution of metal acetate in ethanol was added to the condensed solution. Within a few minutes' crystals of metal benzoin thiosemicarbazone [black crystal for $Ni(BTSC)_2$and grey crystals for $Co(BTSC)_2$] were obtained. The crystals were then recrystallized twice, dried in an oven at 50°C and stored in a desiccator.

Characterization of the synthesized compounds

The synthesized compounds were characterized by taking melting point by using an electro thermal melting point apparatus. Elemental analytical data were determined by using Perkin Elmer 2400 CHNS/O elemental analyzer at BCSIR laboratory, Dhaka. The metals were determined by using Atomic Absorption Spectrometer at Department of Soil, Water and Environment, University of Dhaka.IR spectral data were obtained from central science laboratory, Rajshahi University as KBr disc by using Shimadzu FTIR spectrometer.

Pesticidal screening

Culture of test insect T. castaneum

Mass cultures were maintained in plastic containers (1200ml) and sub-cultures in beakers (1000 ml) with the food medium. The beakers were kept in an incubator at 30°C ± 0.5°C without light and humidity control. Each container and beaker contained 250g and 150g of food respectively. About 200 adult insects in each container and 100 adult insects in each beaker were introduced.

The cultures were checked in regular intervals and eggs and larvae were separated to increase properly. A crumpled filter paper was placed inside each container and beaker for easy movement of the beetles. The containers and beakers were covered with pieces of muslin cloth tightly fixed with the help of rubber bands to avoid possible escape of the beetles.

Preparation of food medium

The whole-wheat flour was used as the food medium for the insect species. The flour was sterilized at 60°C for 24 hours in an oven. A standard mixture of whole wheat flour with powdered dry yeast in a ratio of 19:1 was used(Park *et al.*, 1948) as food medium throughout the experimental period. Both the flour and the powdered dry yeast were sterilized at 60°C for 36 hours in an oven. Food was not used until at least 15 days after sterilization to allow its moisture content to equilibrate with the environment (Khan *et al.*, 1981).

Collection of eggs

About 500 beetles were placed in a 500ml beaker containing food medium. The beaker was covered with a piece of cloth and kept in an incubator at 30°C ± 5°C. In regular interval the eggs were collected by sieving the food medium by two sieves of 500 and 250 meshes separating the adults and eggs respectively following the methods of (Khan and Selman, 1981). Eggs were then transferred to Petri dish (90mm in diameter) and incubated at the same temperature.

Collection of newly hatched larvae

After 3-5 days, the newly hatched larvae were collected with a fine pointed camel hair brush and then shifted to the fresh food medium for culture. The larvae are yellowish white in color and long cylindrical shape. It appears 1mm in length after hatching and become 6-7mm at maturation.

Collection of adults

A huge number of beetles were thus reared to get a regular supply of the newly formed adults. When sufficient adults produced in the sub-cultures, they were collected from the food medium. For this purpose, some pieces of filter paper were kept inside the beaker on the food. Adults crawled upon the paper and then the paper was taken out with some forceps. Beetles were then collected in a small beaker (100ml) with the help of a fine camel-hair brush.

Application of doses in the surface film test

To conduct surface film activity test 60 mm petridishes were taken for all doses and their replications. One millilitre of each of the doses were poured into the lower part of the petri dish and allowed them to dry out. Being volatile the solvent was evaporated out within a few minutes. Thirty insects were released in each of the treated petri dish. A control experiment by applying the only solvent into the petri dish was also set at the same time under the same condition.

Observation of mortality in surface film tests

After completing all the arrangements treated petri dishes were placed in a secured place at room temperature. The whole experiment was observed from time to time and mortality was observed by every 24h, 48h, and 72h and the data was recorded. A simple microscope was used to check each and every beetle by tracing natural movement of its organs. In some cases, hot needle was taken closer to the bodies (without movement) to confirm their death.

Statistical analysis

Mortality of the treated beetles was recorded after 24h, 48h and 72 hours. Corrected mortality % is calculated using (Abbott, 1985) formula:

$$P_r = \frac{P_o - P_c}{100 - P_c} \times 100$$

Where,

P_r = Corrected mortality (%)

P_o = Observed mortality (%) and

P_c = Control mortality (%), sometimes called natural mortality (%).

Then mortality percentages were subjected to statistical (probit) analysis according to (Busvine,1971) by using 'software' developed in the Department of Agricultural and Environmental Science, University of Newcastle upon Tyne, U.K. No provisional graph or tables were required. Heterogeneity was tested by a chi-squared test.

The programme also calculated confidence limits for LD_{50}. Thedose-mortality relationship was expressed as a median lethal dose (LD_{50}). These data was entered into a linear regression programmed, which fitted a regression line onto a probit log dose concentration graph. Percentage of mortality and dose concentration could be determined from this graph using the probit transformation table (Busvine,1980).

Result and discussion

With the replication of different doses of BTSC, $Co(BTSC)_2$ and $Ni(BTSC)_2$ complex was applied as 0.354mg/cm², 0.708 mg/cm², 1.062 mg/cm², 1.415 mg/cm², 1.769 mg/cm² and the mortality was subjected to probit analysis.

Table 1. Yield percentage and physical characteristics of the schiff base andschiff base Complexes.

Test compounds	Yield in [%]	Melting point/Thermal stability [°C]	Physical Form	Solubility
BTSC	60	150-153	Yellowish white crystalline	Ethanol, methanol, DMSO and acetone
$Co(BTSC)_2$	45	Stable up to ~165	Grey crystalline	Ethanol, methanol, DMSO and acetone
$Ni(BTSC)_2$	50	Stable up to ~155	Black crystalline	Ethanol, methanol, DMSO and acetone

Table2. Elemental analytical data of the schiff base and schiff base complexes.

Compounds		Elemental analytical data in [%]					
		C	H	N	O	S	Metal
BTSC	Found	62.78	5.27	14.50	5.30	10.07	
	Theoretical	63.13	5.30	14.72	5.33	10.67	
$Co(BTSC)_2$	Found	39.17	4.01	5.26	20.96	12.55	Co(17.02)
	Theoretical	39.75	4.05	5.15	21.60	13.25	Co(17.13)
$Ni(BTSC)_2$	Found	52.36	4.39	12.21	4.65	9.31	Ni(16.90)
	Theoretical	52.93	4.11	12.44	4.67	9.98	Ni(17.08)

Table 3. IR spectral data of the schiff base and schiff base complexes

Compounds	$\upsilon(NH_2)$	υ(N-H)	υ(C=N)	υ(C=S)	υ(NH-C=S)	υ(M-O)	υ(M-N)	υ(M-S=C)
BTSC	------	3379 w	1682 s	1263 w	977 s	------	-------	------
$Co(BTSC)_2$	3339 w	-------	1567 w	1135 s	682-1024 Wbr	617 s	526 m	427 s
$Ni(BTSC)_2$	3415 s	------	1566 s	1078 s	679-1029 Wbr	617 s	524 w	481 s

[s= strong, w= weak, m= medium, br= broad].

The probit mortality of test compounds on adult *Tribolium castaneum* after 24, 48 and 72 hours of treatment was recorded in Table 4.

In case of BTSC the 95%, confidence limits are 1.24178 to 9.001654mg/cm², 0.7782544 to 1.275247mg/cm² and 0.516194 to 0.9200975mg/cm² after 24, 48 and 72 hours of treatment respectively.

The regression equations are Y = 3.021065 + 1.298358 X, Y = 3.057729 + 1.945466 X and Y = 3.425466 + 1.878195 X after 24, 48 and 72 hours respectively and the χ^2 (chi-squared) value have been calculated as 1.498586, 1.380055 and 5.518341 at three degrees of freedom after 24, 48 and 72 hours respectively. No significant heterogeneities were found.

Table 4. Dose mortality data of the experimental compounds for surface film method to adult *Tribolium castaneum* after 24, 48 and 72 hours of exposure.

Test compound	Time of exposure, hour	Dose, [mg/cm²]	Number of insects used	Number killed	Mortality in [%]	LD_{50} [mg/cm²]
BTSC	24	0.354	30	4	13.33	3.343363
		0.708	30	5	16.66	
		1.062	30	6	20.00	
		1.415	30	9	30.00	
		1.769	30	13	43.33	
		Control	30	0	0.00	
	48	0.354	30	7	23.33	.9962261
		0.708	30	10	33.33	
		1.062	30	14	46.66	
		1.415	30	19	63.33	
		1.769	30	22	73.33	
		Control	30	0	0.00	
	72	0.354	30	9	30.00	.6891654
		0.708	30	15	50.00	
		1.062	30	19	63.33	
		1.415	30	22	73.33	
		1.769	30	24	80	
		Control	30	0	0.00	
$Co(BTSC)_2$	24	0.354	30	5	16.66	1.633098
		0.708	30	8	26.66	
		1.062	30	10	33.33	
		1.415	30	15	50.00	
		1.769	30	16	53.33	
		Control	30	0	0.00	
	48	0.354	30	8	26.66	1.073322
		0.708	30	12	40.00	
		1.062	30	12	40.00	
		1.415	30	18	60.00	
		1.769	30	20	66.66	
		Control	30	0	0.00	
	72	0.354	30	10	33.33	.6237285
		0.708	30	16	53.33	
		1.062	30	19	63.33	
		1.415	30	24	80.00	
		1.769	30	26	86.66	
		Control	30	0	0.00	
$Ni(BTSC)_2$	24	0.354	30	3	10.00	3.344224
		0.708	30	4	13.33	
		1.062	30	7	23.33	
		1.415	30	9	30.00	
		1.769	30	11	36.66	
		Control	30	0	0.00	
	48	0.354	30	6	20.00	1.100927
		0.708	30	9	30.00	
		1.062	30	12	40.00	
		1.415	30	20	66.66	
		1.769	30	20	66.66	
		Control	30	0	0.00	
	72	0.354	30	4	26.66	.8908827
		0.708	30	12	40.00	
		1.062	30	15	50.00	
		1.415	30	20	66.66	
		1.769	30	22	73.33	
		Control	30	0	0.00	

Table 5. LD_{50}, 95% confidence limits, regression equations and χ^2 (df.) values from dose mortality experiment of test compounds against adult *T. castaneum* after 24,48 and 72 hours of exposure.

Test compound	Time of exposure	LD_{50} [mg/cm²]	95% confidence limits		Regression equation	χ^2	df
			Lower	Upper			
BTSC	24 hr	3.343363	1.24178	9.001654	Y = 3.021065 + 1.298358 X	1.498586	3
	48 hr	.9962261	.7782544	1.275247	Y = 3.057729 +	1.380055	3

					1.945466 X		
	72 hr	.6891654	.516194	.9200975	Y = 3.425466 + 1.878195 X	5.518341	3
Co(BTSC)₂	24 hr	1.633098	1.060593	2.51464	Y = 3.126286 + 1.544679 X	.8309689	3
	48 hr	1.073322	.7646816	1.506536	Y = 3.527254 + 1.428838 X	1.5616	3
	72 hr	.6237285	.4706479	.8265995	Y = 3.335755 + 2.093401 X	1.034124	3
Ni(BTSC)₂	24 hr	3.344224	1.357271	8.239939	Y = 2.799204 + 1.443812 X	.5446945	3
	48 hr	1.100927	.8634754	1.403676	Y = 2.874833 + 2.039981 X	2.778469	3
	72 hr	.8908827	.6753811	1.175147	Y = 3.357953 + 1.728797 X	.7756777	3

The regression lines of probit mortality on log dose of BTSC against adult *T. castaneum* after 24, 48 and 72 hours of exposure were shown in figure 2A, 2B and 2C respectively, considerable mortality to the *T. castaneum* adults.

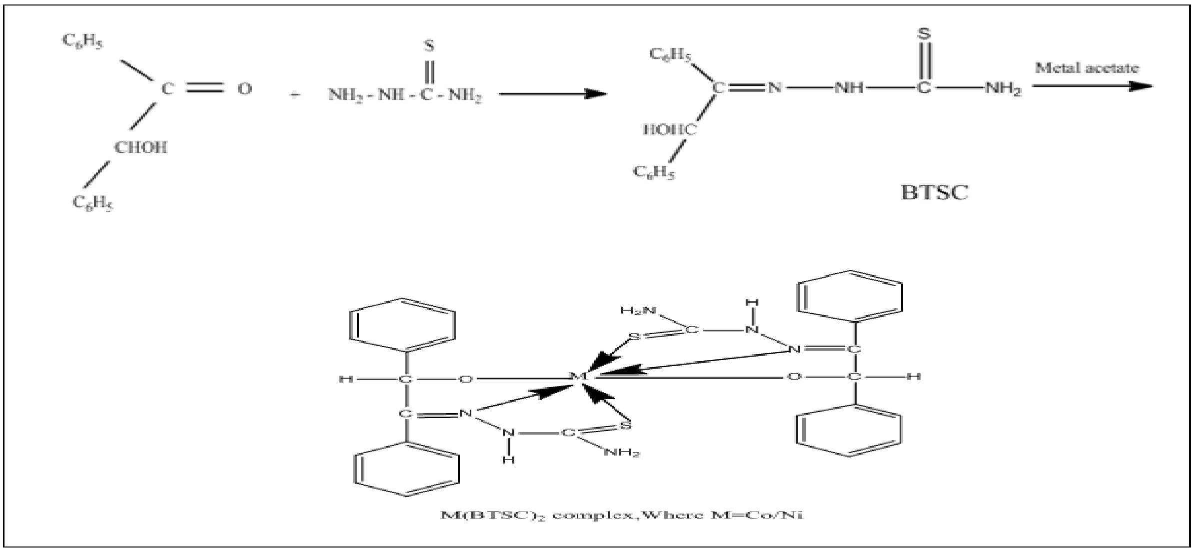

Fig. 1. Synthesis of metal (II)-benzoin thiosemicarbazone complexes,M(II) stands for Co(II)/Ni(II).

In case of $Co(BTSC)_2$ the 95%, confidence limits are 1.060593 to 2.51464mg/cm², .7646816 to 1.506536mg/cm² and .4706479 to .8265995mg/cm² after 24, 48 and 72 hours of treatment respectively. The regression equations are Y = 3.126286 + 1.544679 X, Y = 3.527254 + 1.428838 X and Y = 3.335755 + 2.093401 X after 24, 48 and 72 hours respectively and the χ^2 (chi-squared) value have been calculated as .8309689, 1.5616 and 1.034124 at three degrees of freedom after 24, 48 and 72 hours respectively.

No significant heterogeneities were found. The regression lines of probit mortality on log dose of $Co(BTSC)_2$ complex against adult *T. castaneum* after 24, 48 and 72 hours of exposure were shown in figure 3A, 3B and 3C respectively, considerable mortality to the *T. castaneum* adults.

In case of $Ni(BTSC)_2$ the 95%, confidence limits are 1.357271 to 8.239939mg/cm², .8634754 to 1.403676mg/cm² and .6753811 to 1.175147mg/cm² after 24, 48 and 72 hours of treatment respectively.

The regression equations are Y = 2.799204 + 1.443812 X, Y = 2.874833 + 2.039981 X and Y = 3.357953 + 1.728797 X after 24, 48 and 72 hours respectively and the χ^2 (chi-squared) value have been calculated as .5446945, 2.778469 and .7756777 at three degrees of freedom after 24, 48 and 72 hours respectively.

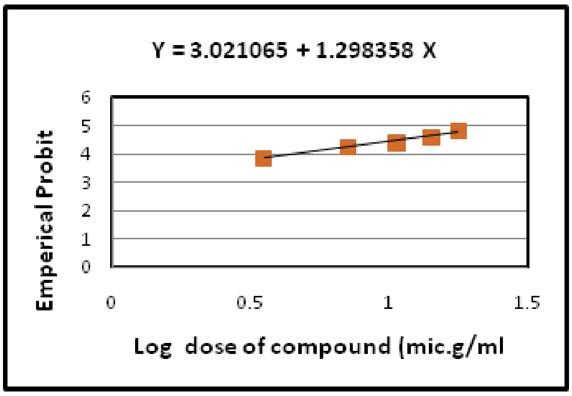

Fig. 2A. Regression line of probit mortality on log dose of BTSC against adult *T. castaneum*after 24 hours of surface film treatment.

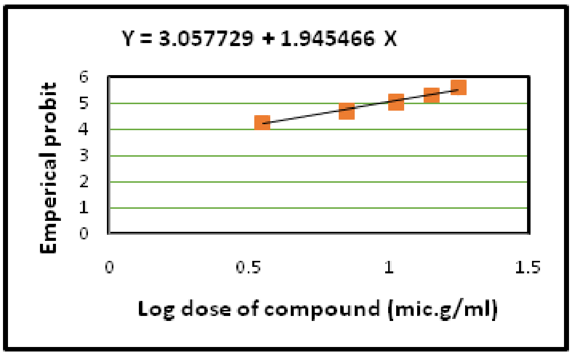

Fig. 2B. Regression line of probit mortality on log dose of BTSC against adult *T. castaneum*after 48 hours of exposure.

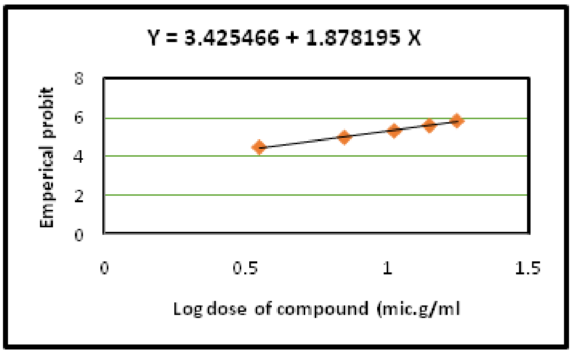

Fig. 2C. Regression line of probit mortality on log dose of BTSC against adult *T. castaneum*after 72 hours of exposure.

No significant heterogeneities were found. The regression lines of probit mortality on log dose of $Ni(BTSC)_2$ complex against adult *T. castaneum* after 24, 48 and 72 hours of exposure were shown in figure 4A, 4B and 4C respectively, considerable mortality to the *T. castaneum* adults.

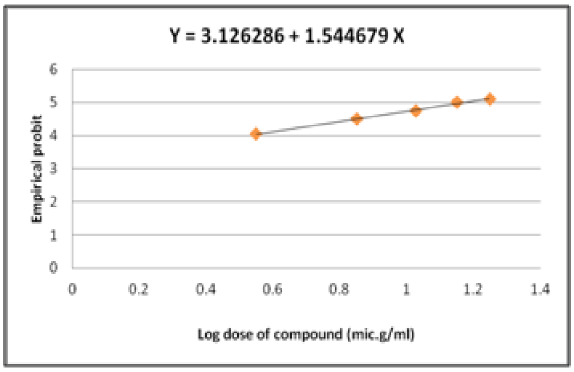

Fig. 3A. Regression line of probit mortality on log dose of $Co(BTSC)_2$ against adult *T. castaneum*after 24 hours of surface film treatment.

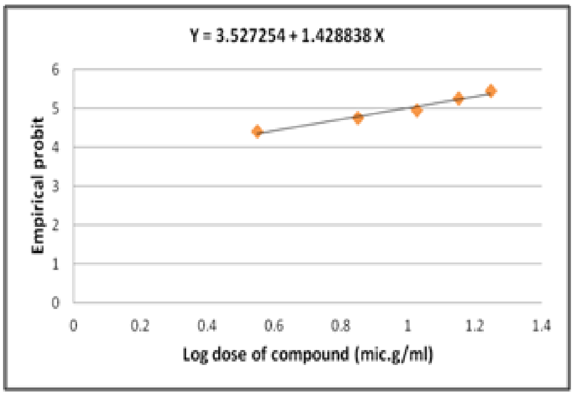

Fig. 3B. Regression line of probit mortality on log dose of $Co(BTSC)_2$ against adult *T. castaneum*after 48 hours of surface film treatment.

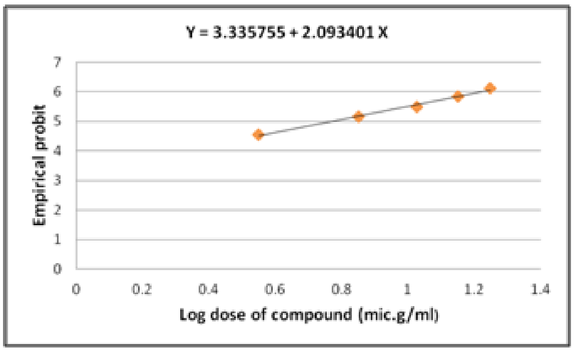

Fig. 3C. Regression line of probit mortality on log dose of $Co(BTSC)_2$ against adult *T. castaneum*after 72 hours of surface film treatment.

It noticed from Table 4 that the LD_{50} values as recorded after 24 hours of treatment were 3.343363, 1.633098 and 3.344224 mg/cm² for BTSC, $Co(BTSC)_2$ and $Ni(BTSC)_2$, respectively as compared with 2.974 µg/cm² for a standard pesticide *malathion*.

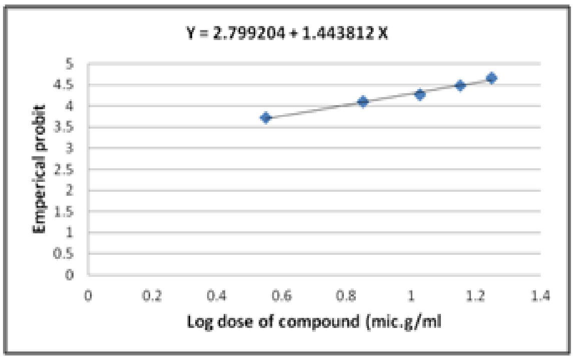

Fig. 4A. Regression line of probit mortality on log dose of $Ni(BTSC)_2$ against adult *T. castaneum*after 24 hours of surface film treatment.

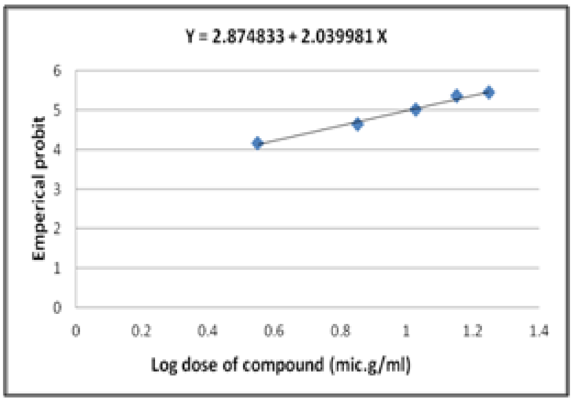

Fig. 4B. Regression line of probit mortality on log dose of Ni(BTSC)2 against adult *T. castaneum* after 48 hours of surface film treatment.

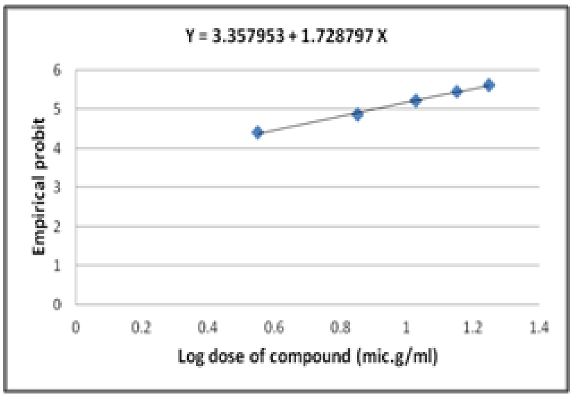

Fig. 4C. Regression line of probit mortality on log dose of $Ni(BTSC)_2$ against adult *T. castaneum* after 72 hours of surface film treatment.

Although these values are comparatively larger than that of the standard pesticide *malathion* but very much alike to those of other schiff base and schiff base complexes studied earlier (Ali *et al.*, 2009). In all cases the mortality percentage increases both with doses of the compounds and duration of this treatment (Table 4).

The Lethal dose, 95% confidence limits and regression equation with χ^2 (df.) values are presented in Table 5 which indicates the good fit of the lines, is found after Probit analysis (GWBASIC PROGRAMING LANGUAGE) 1st release in 1983 and developed in 1988.

Conclusion

Pesticidal activities of the synthesized compounds have been investigated against *Tribolium castaneum* by surface film treatment method. Among the synthesized compounds, it is evident that $Co(BTSC)_2$ complex exhibits a significant pesticidal activity. On the other hand, BTSC and $Ni(BTSC)_2$ complex showed somewhat moderate sensitivity even with higher doses. In the light of the above observations these three compounds may be used as new pesticides. However before assuming so, it is necessary to carry out extensive research works in advanced level.

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