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Advances in Chemical Science
Volume II

Editors:

Dr. Suraj B. Ade

Dr. Omprakash S. Chavan

Dr. Mrs. Arshia Parveen

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Editors

Dr. Suraj B. Ade
Department of Chemistry and Analytical Chemistry,
MSP Mandal's Shri Shivaji College,
Parbhani, M.S.

Dr. Omprakash S. Chavan
Department of Chemistry,
Badrinarayan Barwale College,
Jalna, M.S.

Dr. Arshia Parveen
Department of Chemistry,
B. Raghunath ACS College,
Parbhani, M.S.

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PREFACE

We are delighted to publish our book entitled ***"Advances in Chemical Science Volume II"****. This book is the compilation of esteemed articles of acknowledged experts in the fields of Chemical Science, and allied areas.*

This book is published in the hopes of sharing the excitement found in the research and study of chemical science. Chemical science can help us unlock the mysteries of our universe, but beyond that, conquering it can be personally satisfying. We developed this digital book with the goal of helping people achieve that feeling of accomplishment.

The articles in the book have been contributed by eminent scientists, academicians. Our special thanks and appreciation goes to experts and research workers whose contributions have enriched this book. We thank our publisher Bhumi Publishing, India for taking pains in bringing out the book.

Finally, we will always remain a debtor to all our well-wishers for their blessings, without which this book would not have come into existence.

- Editors

Advances in Chemical Science Volume II

CONTENTS

MODIFICATION IN PROPERTIES OF MAGNESIUM OXYSULFATE BY INCORPORATING STARCH AS AN ADDITIVE

Meenakshi
Department of Chemistry,
University of Rajasthan, Jaipur, Rajasthan, India 302 004
Corresponding author E-mail: meenakshialwaraj@gmail.com

Abstract:

Eco- friendly non calcareous Magnesium oxysulfate cement is first produced by French Engineer Stanislas Sorel in 1867. It is formed by the reaction between MgO and $MgSO_4$. This reaction is exothermic; hence dolomite is used as an inert filler to absorb the excess heat evolved during the reaction. It is used for plastering and decorative purposes (toys and statues), partition walls, preparation of artificial abrasive stones, grinding stones, tiles, light-weight insulating panels etc. It has also got high attenuation power for radioactive emanations. It has no corrosion to steel and effective inhibition of frost. Large scale application of Magnesium oxysulfate is limited due to its low early strength and poor water resistance. Additives may alter the properties of Magnesium oxysulfate cement by forming additional bonds in the matrix. Starch is a dispersible carbohydrate having free hydroxyl groups. In the present study, starch is used as an additive for magnesium oxysulfate cement and the findings are very encouraging. It decreases setting times and improves the mechanical strength and water tightness of the product.

Keywords: Magnesium oxysulfate cement, Setting times, Moisture ingress, Weathering effects, Linear changes, Starch etc.

Introduction:

A binder is a substance that holds or draws other materials together. Chemical binders are substances that can be used directly or indirectly for binding, adhering, or fastening substances (Mathur and Sharma, 2008). Animal or plant glues, polymers, etc. are organic binders which are known as adhesives and lime, cement, gypsum, liquid glass, etc. are known as inorganic binders. Polymerization tendencies or interlocking crystal habits are responsible for their cementing behaviour (Brady, 2002).

Cement is a binder, a substance used in construction that sets, hardens and adheres to other materials, binding them together. Cement is the main component of concrete. It is an economical and high-quality construction material that is used in construction projects worldwide. Various types of cements are known, e.g. Portland cement, Keene's cement, Sorel's cement, ceramic clays etc. (Bonge, 1955; Mills *et al.,* 1955; Leo, 1956). The most common hydraulic cement is Portland cement and others are Pozzolanic cement, masonry cement, sulfate resistant cement etc. (Gillberg *et al.,* 1999; Francis, 1977; Hewpett, 1998). In 1867, a French engineer, Stanislas Sorel, invented non-calcareous cement, named "Sorel's cement." It is also known as Magnesia cement or Magnesium oxysulfate /oxychloride cement.

Magnesium oxysulfate is a non-hydraulic and air-hardening cementing material and it possesses some excellent properties compared with ordinary Portland cement, such as light weight, low thermal conductivity, and fire protection (Beaudoin and Ramachandran, 1977; Newman, 1964; Matkovic *et al.,* 1977; Bensted and Barnes, 2002; Chandrawat and Yadav, 2000).

It has no corrosion to steel and effective inhibition of frost (Yang *et al.,* 2014). In the USA and Europe, the major use of magnesium oxysulfate cement is in the manufacture of light-weight insulating panels (Marmorato and Gladis, 2014). The resistance of Magnesium oxysulfate cement to abrasion is about 1.5 times that of Portland cement (Singh *et al.,* 1997). It is also considered for nuclear applications (Wilson and Nicholson, 2009).

For many years, Magnesium oxysulfate cement has been used in the commercial production of decorative materials, light-weight thermal insulating materials and fire-proof materials (Yang *et al.,* 2014), Gomes and Camarini, 2014; Qin *et al.,* 2018; Newman, 1964). Magnesium oxysulfate cement is less damaging to steel reinforcement and it has superior resistance to weather compared with magnesium oxychloride cement (Walling and Provis, 2016).

The production of lightly burnt magnesium oxide, which is used in Magnesia cement, necessitates a much lower calcination temperature than that required for Portland cement, resulting in significant energy savings (Li *et al.,* 2010; Schollbach and Pollmann, 2011). It is formed by mixing proper ratios of MgO powder with a concentrated solution of $MgSO_4$. This process is exothermic, and the heat evolved during the reaction makes cracks and makes the product unsound. Hence, dolomite is used as inert filler in the matrix to absorb the heat.

The setting and hardening properties of Magnesium oxysulfate cement depend on the ternary hydration phases and microstructures (Urwongse and Sorel, 1980). At temperatures from 30°C to 120°C, following Magnesium oxysulfate phases existing in the Magnesium oxide–

Magnesium sulfate–water ($MgO–MgSO_4–H_2O$) system are $3Mg(OH)_2·MgSO_4·8H_2O$ (3·1·8 phase), $5Mg(OH)_2·MgSO_4·8H_2O$ (5.1.8 Phase) $5Mg(OH)·MgSO_4·3H_2O$ (5·1·3 phase), $Mg(OH)_2· 2MgSO_4·3H_2O$ (1·2·3 phase) and $Mg(OH)_2·MgSO_4·5H_2O$ (1·1·5 phase) (Demediuk and Cole, 1957). 3.1.8 and 5.1.8 are the main strength phases formed in Magnesium oxysulfate cement (Newman, 1964; Kahle, 1972; Urwongse and Sorel, 1980; Mathur and Sharma, 2008; Gomes and Camirini, 2014).

Magnesia cement has a lot of good engineering and mechanical features, but it is challenging to use on a wide scale because of its weak water resistance, which causes the hardened paste to lose a lot of strength in water (Chandrawat *et al.,* 2011; Chau *et al.,* 2009; Chuanmei and Dehua, 1995; Sglavo *et al.,* 2011). Poor water resistance is a drawback of Magnesium oxysulfate cement, which leads to significant moisture absorption and high structural deformability. Starch is a polysaccharide comprising of glucose monomers joined by alpha1, 4 linkages. The simplest form of starch is the linear polymer amylose, also known as amylopectin in its branched form.

The objective of the study is to determine the effect of starch on setting times, weathering effects, moisture ingress, compressive strength, and linear changes in Magnesium oxysulfate cement.

It is found that incorporation of the starch in the matrix makes the product more sound and increases compressive strength of the product.

Materials:

The raw materials needed in the preparation of Magnesium oxysulfate cement trial blocks are Magnesium oxide, Magnesium sulfate, Dolomite (inert filler) and Starch.

(A) Magnesium oxide (MgO): It is a white, light powder and it is the basic raw material for the preparation of Magnesium oxysulfate cement and is procured from Suksha Exports, Bagru, Jaipur. The chemical analysis of MgO is as follows:

$MgO=82.70\%$, $SiO_2=8.51\%$,$CaO=2.80\%$,$Fe_2O_3=0.12\%$,$Al_2O_3=0.07\%$,$LOI=4.40\%$

(B) Magnesium sulfate ($MgSO_4.7H_2O$, Epsom salt): Magnesium sulfate is used to prepare gauging solution in the production of Magnesium oxysulfate cement. Pure and technical grade are the two grades of Magnesium sulfate according to Indian Standard Specifications. In the present research, technical grade Magnesium sulfate is used to prepare oxysulfate cement. Epsom salt is collected from Goodwill Rasayan Jaipur (Raj.).The chemical analysis of Magnesium sulfate is as follows:

$MgSO_4$=96.80%, Fe_2O_3=0.02%, Al_2O_3=0.07%, CaO=1.40%, Moisture=0.98%, Acid insoluble=0.11%

(C) Inert Filler Dolomite ($MgCO_3.CaCO_3$) :- Dolomite powder was used as an inert filler in the preparation of oxysulfate cement. It was procured from M.I.A. Alwar (Raj.). It absorbs the heat evolved during the exothermic formation of Magnesia cement. The chemical analysis of Dolomite is as follows:

SiO_2=5.06%,CaO=29.40%,MgO=19.50%,Fe_2O_3=0.82%,Al_2O_3=0.23%,

LOI=44.50%,$CaCO_3$=52.50%,$MgCO_3$=40.95%, Brightness=93.00%,Whiteness=95.30%

Methods:

All the experiments were carried out on the best Magnesium oxysulfate cement composition (MgO: Dolomite is in a 1:1 proportion, and the density of the gauging solution is 25^0Be) under the same temperature (30^0C) and humidity conditions (above 90 percent). The effects of starch on Magnesium oxysuphate cement were investigated in the following experiments.

1) **Setting Time Investigations:** The effect of Starch on setting characteristics of Magnesium oxysulfate cement was studied by admixing Starch in the dry mix in varying proportions. The quantity of additive was calculated by weight of Magnesia. Wet mixes were prepared by gauging 1:1 dry mixes (by weight of Magnesia and Dolomite) having different quantities of additive with Magnesium sulfate solution of 25^0 Be. The volume of gauging solution was kept constant for each lot of dry-mix. Standard procedures were adopted according to IS Specification to determine standard consistency, initial and final setting times by using Vicat needle apparatus. Findings are summarized in Table1.
2) **Weathering Investigations:** Setting time investigation blocks were used for this test. Weights of the trial blocks were measured after different time interval (24 hrs, 7 days, 30 days and 45 days) with the help of standard chemical balance. The weight of blocks may increase or decrease with time due to different weathering effects. Results are recorded in Table 2.
3) **Moisture Ingress Investigations:** Soundness of the product can be ascertained by this test. After 2 months of curing in identical conditions, setting time investigation blocks were exposed to steam/ boiling water in identical conditions for at least 30 hours. The effect is noted after an interval of five hours. Moisture ingress and soundness are inversely proportional. Results are shown in Table 3.
4) **Compressive Strength Investigations:** Trial blocks of 70.6 mm x 70.6mm x 70.6mm side and 50cm^2 surface area were prepared for the investigation and these were cured for 28 days

under identical conditions of temperature and humidity and then these are tested on compressive strength testing machine. Results are summarized in Table 4.

5) **Linear Change Investigations:** Trial blocks were prepared from standard sized moulds (200mm x 25 mm x 25 mm) and these blocks were kept under 90% relative humidity and 30 $\pm$ 2^0C temperature for 24 hrs. The initial length of the trial blocks can be determined by the micrometer scale. These blocks were cured for 28 days under identical conditions and then the length was measured. This is the final length of the beams. Difference between initial and final length tells the linear change. The greater the change the lesser will be the soundness of the product. Results are recorded in Table 5.

Results and Discussions:

The effect of admixing starch in the matrix on setting characteristics of Magnesia cement is summarized in Table 1. Formation of intercrossing system between oxysulfate cement and starch (eq. v) are responsible for fast setting process hence initial as well as final setting time decreases.

The uncombined residual water present in the matrix after final setting, evaporates with passage of time causing decrease in weights of the trial blocks as is evident from the data recorded in Table 2.

Table 3 reflects the effect of starch on moisture ingress characteristics of oxysulfate cement. Water-tightness of the cement is improved on account of increasing cross interlacing between Magnesium oxysulfate and Starch with increasing additive proportions as Starch is a molecule having free hydroxyl groups which promotes cross interlacing as discussed above (eq. v).

The effect of starch on compressive strength of oxysulfate cement isenumerated in Table 4. Increasing proportions of the additive increases compressive strength of the cement. Formation of intercrossing system between Magnesia cement and Starch is responsible for this increase.

Changes in the lengths of the trial beams after incorporating Starch were recorded in Table 5. Due to interlinking of crystals a sound structure is formed, hence insignificant volume changes are observed.

The above discussion can be explained by following chemical reactions:-

$CaO + H_2O \longrightarrow Ca(OH)_2$ ----------(i)

$MgO + H_2O \longrightarrow Mg(OH)_2$ ----------(ii)

$3Mg(OH)_2 + MgSO_4 + 8H_2O \longrightarrow 3Mg(OH)_2MgSO_4.8H_2O$ -----(iii)

(3.1.8 Form)

Magnesium oxysulfate cement

$5Mg(OH)_2 + MgSO_4 + 8H_2O \longrightarrow 5Mg(OH)_2MgSO_4.8H_2O$ -------(iv)

(5.1.8 Form)

Magnesium oxysulfate cement

Starch + MOS + Starch ⟶ Starch | MOS | Starch ----------(v)

MOS = Magnesium oxysulfate cement

Table 1: Effect of Starch on setting characteristics of Magnesium oxysulfate

Sr.No.	(% of Starch in dry-mix composition)	Setting time	
		Initial (min)	Final (min)
1.	0%	70	210
2.	5%	53	145
3.	10%	47	132
4.	15%	45	118
5.	20%	41	116

Table 2: Effect of Starch on weathering characteristics of Magnesium oxysulfate

Sr. No.	(% of Starch in dry-mix composition)	Weight of blocks in gm after			
		24 hrs	7 days	30 days	45 days
1.	0%	259.05	255.39	252.87	252.07
2.	5%	261.84	256.44	253.57	251.83
3.	10%	251.73	245.77	242.98	241.78
4.	15%	248.37	242.19	239.74	238.62
5.	20%	247.49	241.84	239.35	238.43

Table 3: Effect of Starch on moisture ingress characteristics of Magnesium oxysulfate

Sr. No.	(% of Starch in dry-mix composition)	Trial blocks kept in boiling water for					
		0-5 hrs	5-10 hrs	10-15 hrs	15-20 hrs	20-25 hrs	25-30 hrs
1.	0%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
2.	5%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
3.	10%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
4.	15%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.
5.	20%	N.E.	N.E.	N.E.	N.E.	N.E.	N.E.

N.E. = No Effect

Table 4: Effect of Starch on compressive strength of Magnesium oxysulfate

Sr. No.	(% of Starch in dry-mix composition)	Compressive strength (kg/cm^2)
1.	0%	260.530
2.	5%	270.541
3.	10%	274.549
4.	15%	282.565
5.	20%	298.597

Table 5: Effect of Starch on linear changes of Magnesium oxysulfate

Sr. No.	(% of Starch in dry-mix composition)	Length of beams (mm)		Change in length (mm)
		Initial	Final	
1.	0%	200.00	199.980	0.020
2.	5%	200.00	199.970	0.030
3.	10%	200.00	199.934	0.066
4.	15%	200.00	199.954	0.046
5.	20%	200.00	199.936	0.064

Conclusions:

1) Starch decreases initial as well as final setting time of Magnesium oxysulfate cement.
2) Starch improves water-tightness of the final product.
3) Mechanical strength of Magnesium oxysulfate is also improved by starch.
4) Insignificant linear changes are observed in the beams after admixing Starch in the matrix.

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A SIMPLE AND EFFICENT METHOD FOR OXIDATION OF SOME ALCOHOLS BY QUINOXALINUM BROMOCHROMATE

Sandeep V. Khansole* and Shivraj B. Sirsat

Department of Chemistry,

Yeshwant Mahavidyalaya, Nanded, MS 431 603

*Corresponding author E-mail: sandeepkhansole@yahoo.com

Abstract

Quinoxalinum bromochromate is an efficient reagent for the oxidation of various alcohols.This is the stable, mild, non hygroscopic, selective oxidizing agents and capable of oxidizing all functional groups.The advantages of this reactant are higher yield of product, better selectivity, milder conditions of oxidation. We have used this reagent for the oxidation of various alcohols and obtained product in good yield and short period of time.

Introduction:

A variety of compounds containing chromium (VI) have established as a versatile oxidant for many types of substrates varying from metal ions to naturally occurring organic compounds, and has a wide range and applications spanning the synthesis of sulphur nanoparticals[1] and determination of biological oxygen demand in organic polluted water. Before the discovery of onium chromates or dichromates, water soluble potassium or sodium dichromates were in use with strong acid as oxidants and, in most cases the products were nonspecific. The first attempt to make the reagent mild was reported by Sarett and coworker, who used pyridinium to form a salt with CrO_3, a Lewis acid, in order to oxidize some steroidal alcohols[2]. This reagent was subsequently used by various workers without analyzing the structure of oxidant[3]. Corey, in his novel attempt to establish pyridinium chlorochromate[4] as a versatile oxidant, revisited Sarett's reagent and discovered it to be pyridinium dichromate[5]. The development of newer chromium (VI) reagents for the oxidation of organic substrates continues to be of interest. Halochromates have been used as mild and selective oxidizing reagent in synthetic organic chemistry.

A number of new chromium containing compounds like pyridinum bromochromate[6], Quinoxalinum chlorochromate[7], 2,2' bipyridinium chlorochromate[8], pyridinium

fluorochromate[9], Quinoxalinum fluorochromate[10], Quinoxalinum bromochromate[11] Quinoxalinum dichromate[12], imadazolium fluorochromate[13] have been used to study the oxidation of various organic compounds. The kinetics and mechanism of oxidation of Cr(VI) has been well studied, chromic acid being one of the most versatile available oxidizing reagents, reacting with diverse substrates.

The present research proposal deals with the synthetic applications of some nonconventional chromium (VI) oxidants having heterocyclic bases.

Objective of present work:

The objectives of proposed work are:

a) To synthesize the some halochromate having heterocyclic bases, which will act as oxidizing agents.
b) To study the oxidation of some aromatic and aliphatic compounds by halochromates having heterocyclic bases

Advantages of halochromate reagents are as follows

i) Capable of oxidizing all functional groups
ii) These are the mild and selective oxidizing agents
iii) Quaternary ammonium salt is used as phase transfer catalyst hence oxidizing reagents are efficient
iv) It may be used as crystal growth agents which improves the quality of crystals
v) Lower cost, higher yield, better selectivity, milder conditions.

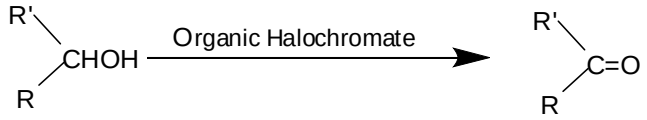
Experimental:

1. Method of Preparation of Quinoxalinum bromochromate

Chromium trioxide (20 g, 0.2 mol) was dissolved in water (25 ml) and cooled to 0^0C.To this solution hydrobromic acid (40%, 23.5 ml, 0.2 mol) was added drop wise during 10 min .To this resulting solution quinoxaline (27 g,0.2 mol)was added and then cooled for 2hr and filtered. The resulting mustered yellow crystal were dried and recrystallized. The purity of sample checked by iodometric method. The reagent had of 108-110^0C melting point and molecular formula [C8H6N2 $HCrO_3$-Br]

2. General method of oxidation of alcohols

A mixture of substrate (1mmole) in CH_2Cl_2 and QxBC (1mmole) was dissolved in a small amount of the solvent. The mixture was stirred for 1 to 1.5 h at room temperature. The progress of the reaction was monitored by TLC or GC. The mixture was extracted with CH_2Cl_2 or ether and filtered through a silica gel or alumina pad. The solvent was evaporated and the resulting crude material was purified on a silica gel column with appropriate eluent to afford the pure product.



R and R'= H,CH_3,OCH_3,Cl

3. Product of oxidation of alcohols by QxBC

Sr. No.	Alcohols	Product	BP ^{0}C Reported
1	Benzyl alcohol	Benzaldehyde	178
2	n propyl alcohol	Propanal	49
3	Iso propyl alcohol	Acetone	56
4	Amly alcohol	1-pentynal	105
5	Iso amyl alcohol	2 pentanone	102
6	n butyl alcohol	1-butanal	75
7	Iso butyl alcohol	2 butanal	78
8	N hexyl alcohol	1 hexanal	130

Conclusion:

The synthesized quinoxalinum bromochromate reagent is found to be very efficient reagents for the oxidation of various alcohols. The method of synthesis of reagent is easy and method of oxidation used for alcohols issimple. The lower acidity of this reagent, the ready preparation, its stability, no hygroscopic in nature is the advantages of reagent.

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TOXICITY, MODE OF ACTION OF CHLORANTRANILIPROLE AND ITS EFFECTS ON NON-TARGET ORGANISMS

Vinod Kumar Dubey*[1] and Kavita Jain[2]

[1]Department of Entomology, Post Graduate College of Agriculture,
Dr. Rajendra Prasad Central Agricultural University,
Pusa, Samastipur, (Bihar) 848125

[2]Division of Nematology, Indian Agricultural Research Institute,
Pusa, New Delhi-110012

*Corresponding author E-mail: vinodkumardubey42@gmail.com

Introduction:

Impact of green revolution paved way for modern agriculture satisfying the needs of increasing population by increased food production and productivity. On the other hand, this modern agriculture also introduced Effective plant protection chemicals and fertilizers along with high yielding varieties. Chemical control has become an indispensable tool for agricultural pest management in the present-day situation. And also, widespread use of broad-spectrum insecticides leads to development of insecticide resistance, which is a trending problem. And that is the reason why insecticides with newer mode of action are desired, and developing the same is again a challenging task for researchers. Diamides are one such group of insecticides with unique mode of action, chemistry and biological features. Here with we discussed about one of the diamide insecticides with outstanding biological attributes, the chlorantraniliprole and its effects on non-target organisms.

The diamides are the most recent addition to the limited number of insecticide classes with specific tar-get site activity that are highly efficacious, control a wide pest spectrum, and have a favorable toxicological profile. Currently available diamide insecticides include chlorantraniliprole and flubendiamide, with cyantraniliprole already being sold in some countries as launch progresses. Flubendiamide, the first diamide insecticidal compound, was discovered by Nihon Nohyaku and co-developed with Bayer. due to the value provided by the diamides, growers are rapidly adopting these products at the risk of excluding the use of alternate-chemistry insecticides in resistance management rotation schemes. DuPont commercializes chlorantraniliprole and cyantraniliprole under the technical trade names Rynaxypyr™ and

Cyazypyr™ and has a major interest in preserving diamide efficacy. Diamides are the selective broad-spectrum insecticides. Chlorantraniliprole, is a new compound developed and marketed by E. I. DuPont de Nemours and Company which belongs to chemical class anthtranilic diamides having the molecular formula "$C_{18}H_{14}BrCl_2N_5O_2$". Its DuPont registered trademark (active) is Rynaxypyr®.

In India it is marketed with two formulations, *viz*.,

(a) Chlorantraniliprole 18.5 SC

(b) Chlorantraniliprole 0.4 G

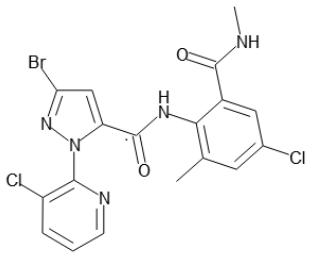
Along with these there is one more formulation yet to introduce in the market, which is formulated for seed treatment- Chlorantraniliprole 625 FS.

General features of chlorantraniliprole

- It's a contact and stomach poison, primarily effective on ingestion secondarily after contact.
- Chlorantraniliprole has a novel mode of action which activates the arthropod ryanodine receptor (RyR).
- Its primarily developed for management of lepidopteran pests.
- It is efficacious on most lepidopterans and selected species of diptera and coleoptera.
- Safe to mammals and beneficial organisms (predators, parasitoids, pollinators and many other soil invertebrates).
- Diamides are specially developed to tackle the widespread insecticide resistance problems.

Chemical features of chlorantraniliprole

- Its IUPAC name is 3-bromo-4'-chloro-1-(3-chloro2-pyridyl)-2'-methyl-6'-(methylcarbamoyl) pyrazole-5-carboxanilide.
- Molecular weight: 483.1 g/mol.
- Molecular formula: $C_{18}H_{14}BrCl_2N_5O_2$
- pH: 5.77 at 20°C
- Water solubility: 0.9-1.0 mg/L at 20°C
- Melting point: 208-210°C
- Dissociation Constant: 10.88
- Viscosity: Its highly viscous.



$C_{18}H_{14}BrCl_2N_5O_2$

Key biological attributes of chlorantraniliprole

- **Unique mode of action**: Till now whatever the insecticides we are having in the market are of nervous system mode of action. Chlorantraniliprole is having very unique mode of action that is it blocks the ryanodine receptors of insect muscle cells, there by killing insect by sustained muscle contraction and paralysis.
- **Differential selectivity towards non target organisms:** It explains about its specific selectivity of only the insect ryanodine receptors over mammalian ryanodine receptor.
- **Long-lasting activity against target pest species:** When applied over a crop it remains for longer period of time thus providing safety against pests even during later stages of the crop.
- **Quick feeding cessation:** After synthetic pyrethroids and fast acting carbamates, diamides are the third fastest acting insecticides, where they inhibit feeding very quickly after ingestion.
- **Safe toxicological and eco-toxicological profile:** Here safe toxicology indicates its safety towards mammals and safe eco-toxicology means its safety towards the ecosystem.
- **Very specific in action:** It targets only the ryanodine receptors without affecting any other physiological processes of the insect.
- **Having green label- toxicity symbol:** Till now we are having very few green label insecticides namely, flubendiamide, cyantraniliprole, spinetoram, novaluron and chlorantraniliprole indicating its safe nature towards human beings.

- **Higher efficacy at low doses:** Chlorantraniliprole is recommended at very low dosages with which it shows excellent insecticidal activity.
- **Reduced risk pesticides**: It is classified as safer insecticide by Environmental protection agency of USA (EPA, 2008).

Origin and History of chlorantraniliprole

- 1993- During synthetic research program in Japan, the scientists of Nihon Nohyaku private limited were engages themselves in developing as herbicide named ‘Pyrazin dicarboxamide’
- They came up with an intermediate product called **Benzene dicarboxamide**, which was having some amount of insecticidal activity.

- Optimization of this transient compound with pthalic acid lead to discovery of "Flubendiamide" during 1998.
- 1998- Flubendiamide is known as the first ever developed diamide insecticide, which is developed with special toxicity towards lepidopteran crop pests.
- 2007- Bayer crop science AG in collaboration with Nihon Nohyaku Pvt. Ltd. launched the flubendiamide into the market under the trade name "Fame".
- 2004-05- Looking into the potential insecticidal activity of flubendiamide, DuPont researchers explored one more outstanding molecule by replacing pthalic acid with anthranilic acid.
- 2008- This transformation lead to development of the first anthranilic diamide called "chlorantraniliprole".
- Immediately after its discovery they lauched this product into the market with DuPont registered trade name **Rynaxypyr** in 2008.
- Presently its available with the famous brand of DuPont i.e **Coragen**
- Thinking this as an important lifesaving discovery the scientists behind this discovery are awarded as **the heroes of chemistry** by Americal chemical society in 2013.
- The scientists behind the discovery of chlorantraniliprole are:
- Daniel cordova, George P. Lahm, Thomas P. Selby, Thomas Stevenson and John Freudenberger and they belong to DuPont de Nemours and Company.

Classification of diamides

Diamides are broadly categorized into two groups namely,

i. Pthalic diamides
ii. Anthranilic diamides

Pthalic diamides

Phthalic acid is an aromatic dicarboxylic acid, with formula $C_6H_4(CO_2H)_2$. It is an isomer of isophthalic acid and terephthalic acid. Although phthalic acid is of modest commercial importance, the closely related derivative phthalic anhydride is a commodity chemical produced on a large scale.

Phthalic acid diamides activate ryanodine-sensitive intracellular calcium release channels (ryanodine receptors, RyR) in insects. With Ca^{2+} measurements, we showed that flubendiamide and related compounds induced ryanodine-sensitive cytosolic calcium transients that were independent of the extracellular calcium concentration in isolated neurons from the pes

insect *Heliothis* virescens as well as in transfected CHO cells expressing the ryanodine receptor from *Drosophila melanogaster*.

Ex: Flubendiamide

Anthranilic diamides

Anthranilic acid (*o*-aminobenzoic acid, 2-aminobenzoic acid, 2-AA, 2AA, AA) is an aromatic acid with the formula $C_6H_4(NH_2)(CO_2H)$ and has a sweetish taste.[6] The molecule consists of a benzene ring, *ortho*-substituted with a carboxylic acid and an amine. As a result of containing both acidic and basic functional groups, the compound is amphoteric. Anthranilic acid is a white solid when pure, although commercial samples may appear yellow.

Anthranilic diamides potently activate this receptor, releasing stored calcium from the sarcoendoplasmic reticulum causing impaired regulation of muscle contraction. Expression of a recombinant *Drosophila* ryanodine receptor in a lepidopteran cell line confers sensitivity to anthranilic diamides similar to that observed with native receptors. Ligand-binding studies with radiolabeled ryanodine and radiolabeled anthranilic diamide in *Periplaneta americana* reveal a single, saturable binding site for this chemistry distinct from that of ryanodine.

Ex: This group consists of four molecules, *viz*,

1. Chlorantraniliprole
2. Cyantraniliprole
3. Cyclaniliprole
4. Tetraniliprole

Among these four, only chlorantraniliprole and cyantraniliprole are known to show insecticidal activity, hence these two only are commercially used as potential insecticides.

Crops, target pests and recommended dosage

In India the dosage fixed by CIB and RC will be followed for management of various crop pests. Chlorantraniliprole will be specially recommended for the management of lepidopteran pests of crops.

The recent data on usage of chlorantraniliprole on different crops and waiting period is given below.

Table 1: Crops, target pests and recommended dosage

Crop	Pest	Dosage/hectare		Waiting period (Days)
		g a.i.	Formulation (ml)	
Rice	Stem borer and Leaf folder	30	150	47
Cabbage	Diamond back moth	10	50	3
Cotton	Boll worms and Tobacco caterpillar	30	150	9
Sugarcane	Termite Early shoot borer Top shoot borer	100-125 75 75	500-625 375 375	208
Tomato	Fruit borer	30	150	3
Chilli	Fruit borer and Tobacco caterpillar	30	150	3
Brinjal	Shoot and fruit borer	40	200	3
Pigeon pea	Gram pod borer and Pod fly	50	150	22
Bengal gram	Pod borers	25	125	11
Black gram	Pod borers	20	100	20
Maize	Spotted stem borer, Pink stem borer and Fall armyworm	40	200	10
Ground nut	Tobacco caterpillar	30	150	
Soybean	Green semi-looper, Stem fly, Girdle beetle and Tobacco caterpillar	30	150	29
Okra	Fruit borers	25	125	5

Trade names of chlorantraniliprole

Chlorantraniliprole is commercially available in the market under different trade names with different formulations some of them are given below.

Sr. No.	Trade name	Formulation	Traders
1	Coragen	18.5 SC	DuPont
2	Cover	18.5 SC	ADAMA
3	Premio	18.5 SC	DuPont
4	Vesticor	18.5 SC	BASF
5	Fornax	18.5 SC	Coramandel international Ltd.
6	Enfuse	0.4 GR	ADAMA
7	Ferterra	0.4 GR	DuPont
8	Cosko	18.5 SC	P I Industries

Market overview

This report also studies the global Chlorantraniliprole market status, competition landscape, market share, growth rate, future trends, market drivers, opportunities and challenges, sales channels and distributors. The growth of chlorantraniliprole's sales from 2008 to 2014 led DuPont's crop protection business to grow rapidly. From 2015-2017, sales of chlorantraniliprole have slowed down.About 30% of the quantity produced is used for the rice industry. Soy fruits and vegetables applications and soy applications accounted for 24% and 22% of the share of consumption volumes.

Market segment by application

- Rice
- Soybean
- Fruits and vegetables
- Corn
- Others

Market segment by regions

- United states
- China
- European Union
- Rest of the world (Japan, Korea, India and Southeast Asia)

✓ Expected growth rate for next five years: 5%

✓ Present market share (2019): 1500 million US$

✓ Expected share in (2024): 2020 million US$

Mode of action

Development of insecticides with unique modes of action is necessary to combat widespread insecticide resistance. A new class of insecticides has been discovered, the anthranilic diamides, that provides exceptional control through action on a novel target, the ryanodine receptor. Anthranilic diamides potently activate this receptor, releasing stored calcium from the sarcoendoplasmic reticulum causing impaired regulation of muscle contraction.

This novel insecticide mode of action seems to be restricted to specific ryanodine (RyR) subtypes because the anthranilic acid diamides reported here had almost no effect on mammalian type 1 ryanodine receptors. There are many evidences that phthalic acid and anthranilic diamides activate ryanodine-sensitive intracellular calcium release channels (ryanodine receptors) in insects.

Terminologies

1. **Ca^{2+} homeostasis:** Regulation of concentration of calcium ionsin the extra cellular fluid.
2. **Electrophysiology:** Its an electrical phenomenon associated with nerves.
   Ex.: Conduction of a nerve impulse, neuromuscular contraction.
3. **L-type voltage dependent calcium channels:** These are also calcium release channels located on the plasma membrane of insect muscle cells.
4. **Sarcoplasmic reticulum:** The special endoplasmic reticulum of skeletal muscle cells, that function as calcium storage and release channels.
5. **Glutamate:** Its an excitatory neurotransmitter.
6. **Calcium induced calcium release:** Ryanodine receptors are very much sensitive to calcium concentration inside and outside the muscle cell, hence opening of ryanodine receptor channel based on induced calcium concentration is known as calcium induced calcium release (CICR).
7. **Store overload induced calcium release:** Calcium ions will be released when there will be increase in the concentration of calcium in cytoplasm.
8. **Target site**- Ryanodine receptor

Ryanodine receptor and its types

Ryanodyne: Basically it's an alkaloid, extracted from the roots of a neotropical plant *Ryania speciose*, used earlier as an insecticide but it was withdrawn from use because of its effect on mammalian ryanodine receptors along with arthropods.

Ryanodine receptor: The receptors specific to calcium ion channels which are located on the sarcoplasmic reticulum.

Types of Ryanodine receptors:

There are three types of ryanodine receptors, namely;

Type I: These are located on skeletal muscles.

Type II: These are located on striated muscles.

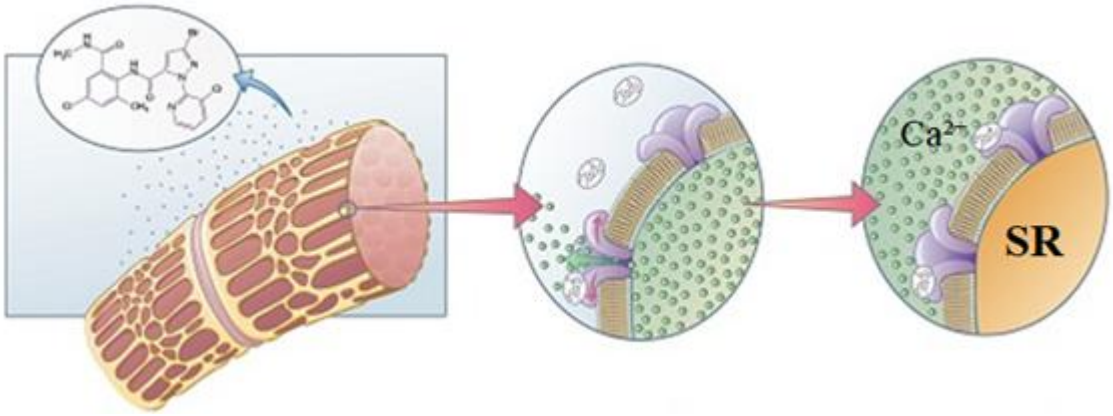
Type III: These are most widely expressed, rarely observed in brain cells.

Chlorantranilprole acts mainly in three steps *viz,*

Phase 1: Exposure phase- Insect comes in contact with or ingests chlorantraniliprole the active ingredient into the body.

Phase 2: Activation phase- Chlorantraniliprole binds to and activates ryanodine receptors located in the insect muscle cells, and causes them to open.

Phase 3: Paralysis and death- Calcium ions flow out of the ryanodine receptors, depleting the calcium required for muscle contraction. Paralysis of the insect muscles leads to death.



Exposure phase **Activation phase** **Paralysis and death phase**

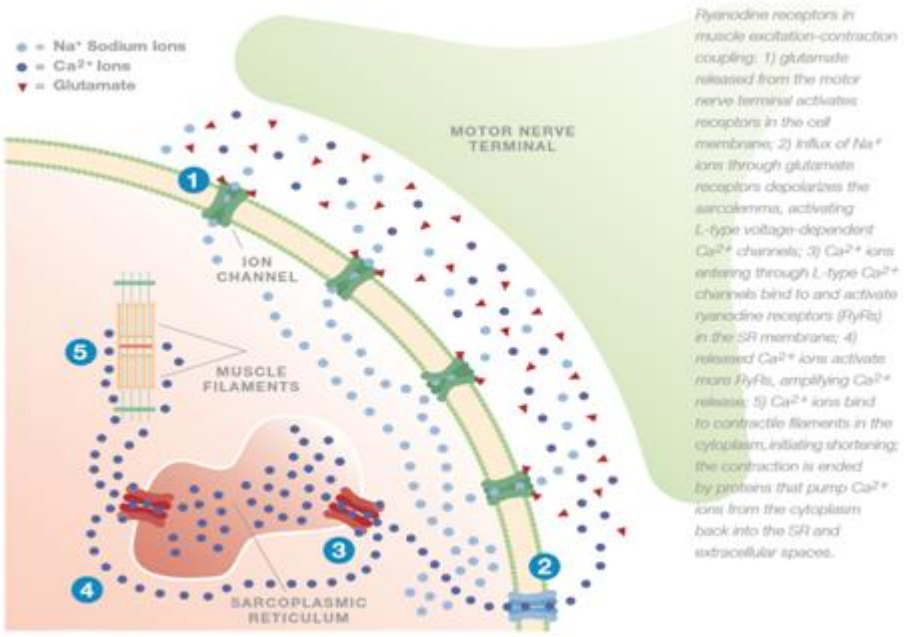
Neuromuscular Transmission and Excitation-Contraction Coupling:

The last process required for understanding insecticide mode of action on nerve and muscle is muscle excitation-contraction coupling. Muscle contraction is ultimately brought about by Ca2+-sensitive contractile proteins in muscle cells that use energy from ATP to cause cell shortening in the presence of cytoplasmic Ca2+ ions. The cytoplasmic free Ca2+ ion concentration in resting muscle cells is maintained at a very low level by ATP-driven pumps in the plasma membrane that pump Ca2+ ions out of the cell, and by similar pumps in the

membrane that encloses an extensive intracellular storage organelle called the sarcoplasmic reticulum (SR), where large amounts of free Ca2+ ions are stored. The SR membrane has a high density of calcium-activated calcium channels called ryanodine receptors (RyRs), which release SR Ca2+ ions into the cytoplasm when activated by cytoplasmic Ca2+ ions, increasing the cytoplasmic Ca2+ ion concentration even further. This inherent positive feedback can produce the rapid rise in cytoplasmic Ca2+ ion concentration needed to activate the contractile proteins in the muscle cell. Diamide insecticides chlorantraniliprole, cyantraniliprole and flubendiamide activate RyRs, inducing muscle contractions.

Neuro inhibition of muscle contraction in insects by chlorantraniliprole:

It's all about the mechanism of excitation-contraction coupling in insect muscle. The command for the muscle to contract is transmitted to the muscle cell from motor neurons. Release of the neurotransmitter glutamate onto the muscle membrane from motor nerve terminals leads to activation of excitatory glutamate receptors, which allow sodium ions to flow into the cell and cause a small depolarization.



This depolarization triggers the activation of L-type voltage-dependent calcium channels in the plasma membrane, which allow enough Ca2+ ions into the cell to activate ryanodine receptors in the sarcoplasmic reticulum membrane, leading to the release of massive amounts of free Ca2+ ions into the cytoplasm from SR stores.

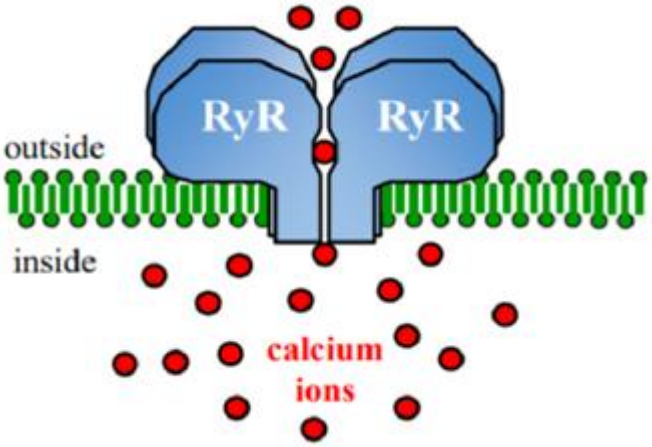
The rise in cytoplasmic Ca2+ ion concentration initiates shortening of muscle contractile filaments, causing the muscle cell to contract, and also activates Ca2+ pump proteins that pump Ca2+ ions back into the SR and into the extracellular spaces, terminating the contraction and

restoring the resting state. It should be noted that the excitatory glutamate receptors in the postsynaptic muscle membrane are not cys-loop receptors and are not targets of any insecticides, in contrast to the GluCIs, which also occur on the muscle membrane, and are targets of avermectins and milbemycins.

Action on Ryanodine receptor function

Chlorantraniliprole activate ryanodine receptor, releasing stored calcium from the sarcoendoplasmic reticulum causing impaired regulation of muscle contraction

Effects on Non-target organisms



Before saying chlorantraniliprole is safe, we need to understand the physiological effect of this chemical in various non target organisms.

Non target organisms include soil invertebrates like springtails, oribatid mites, isopods and earthworms, birds, and aquatic organisms like fishes and marine organisms, also mammals including us, the human beings. Let us study them one by one.

Case studies:

I. Effects on soil invertebrates: Spring tail (*Folsomia candida*)- Lavtizar *et al.*, 2016)

a. Survival and reproduction toxicity test:

The authors conducted an experiment to find out the effect of chlorantraniliprole on survival and reproduction of springtails, *Folsomia candida* during 2016 in Netherlands.

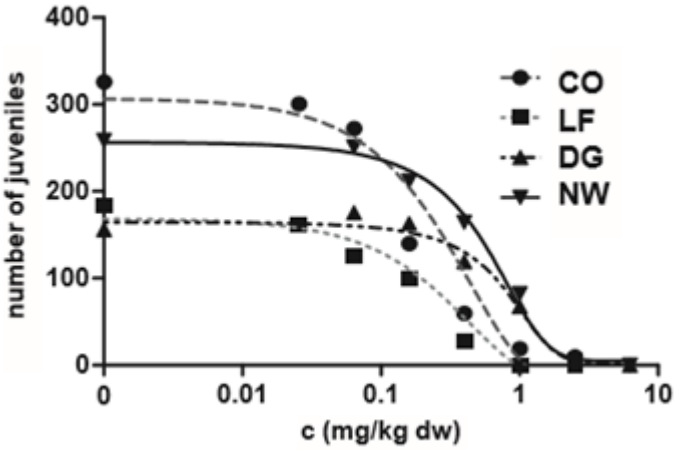
They used four soils having different organic matter content *viz,* Soils with higher organic matter content were:

Coimbra (CO) and Dutch grassland (DG). Soils with lower organic matter content were: Lufa 2.2 (LF) and Northwales (NW).

Methodology

They provided 10 healthy springtails for each plate containing 30g of moist soil. And the soil itself was treated with nominal concentrations of chlorantraniliprole and the same was exposed for 28 days. After 28 days the number of surviving adults and juveniles were recorded.

Results:



Results indicated that Coimbra and Dutch grassland soils did not get affected by chlorantraniliprole with respect to survival and reproduction even at the highest concentrations tested. Where as in *Lufa* and Northwale soils survival decreased in a dose dependent manner, indicating that increase in the organic matter content will tend to reduce the toxicity to springtails.

Reason:

Organic matter content reduces the bio availability of chlorantraniliprole to springtail because of its less water solubility.

b. Avoidance test of *Folsomia candida*:

Methodology:

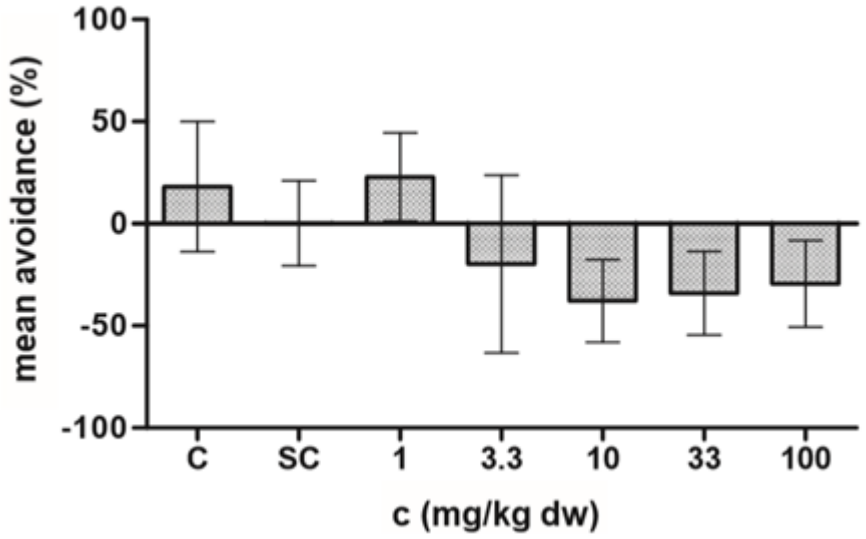
Round test containers with soil divided into two equal halves one containing nominal concentration of chlorantraniliprole and another untreated, each of 15 grams. 7 such concentrations were prepared each of five replications. 20 healthy springtails were placed at central line and containers were closed with lid, and test animals were allowed to choose and stay at the preferred site. After two days, soil again divided into two halves the number of springtails was counted on each side by floatation.

% Mean avoidance is calculated by using the formula:

% Mean avoidance= No. of individuals in control- No. of individuals in treated/ Total number *100

Results:

Animals avoided the soil with lowest chlorantraniliprole concentration measured in mg/kg. At all the higher concentration the attraction towards the treated surface is seen with the net mean negative avoidance of -38 and -29 per cent.



Reason:

Chlorantraniliprole inhibited their locomotor ability and had difficulty in moving.

Conclusion:

Chlorantraniliprole being an important molecule, having unique mode of action and chemistry harming only the target organisms leaving behind the natural enemies and beneficial organism. So we can say it is one of the best fitting insecticide in integrated pest management and integrated resistance management programs.

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FLAVONOIDS AND THEIR ACTIVITY: A MINI-REVIEW

Ajay B. Jadhao
Department of Botany
Arts and Science College, Pulgaon, District - Wardha
(Affiliated By RTM Nagpur University)
Corresponding author E-mail: cyrusajay@gmail.com

Abstract:

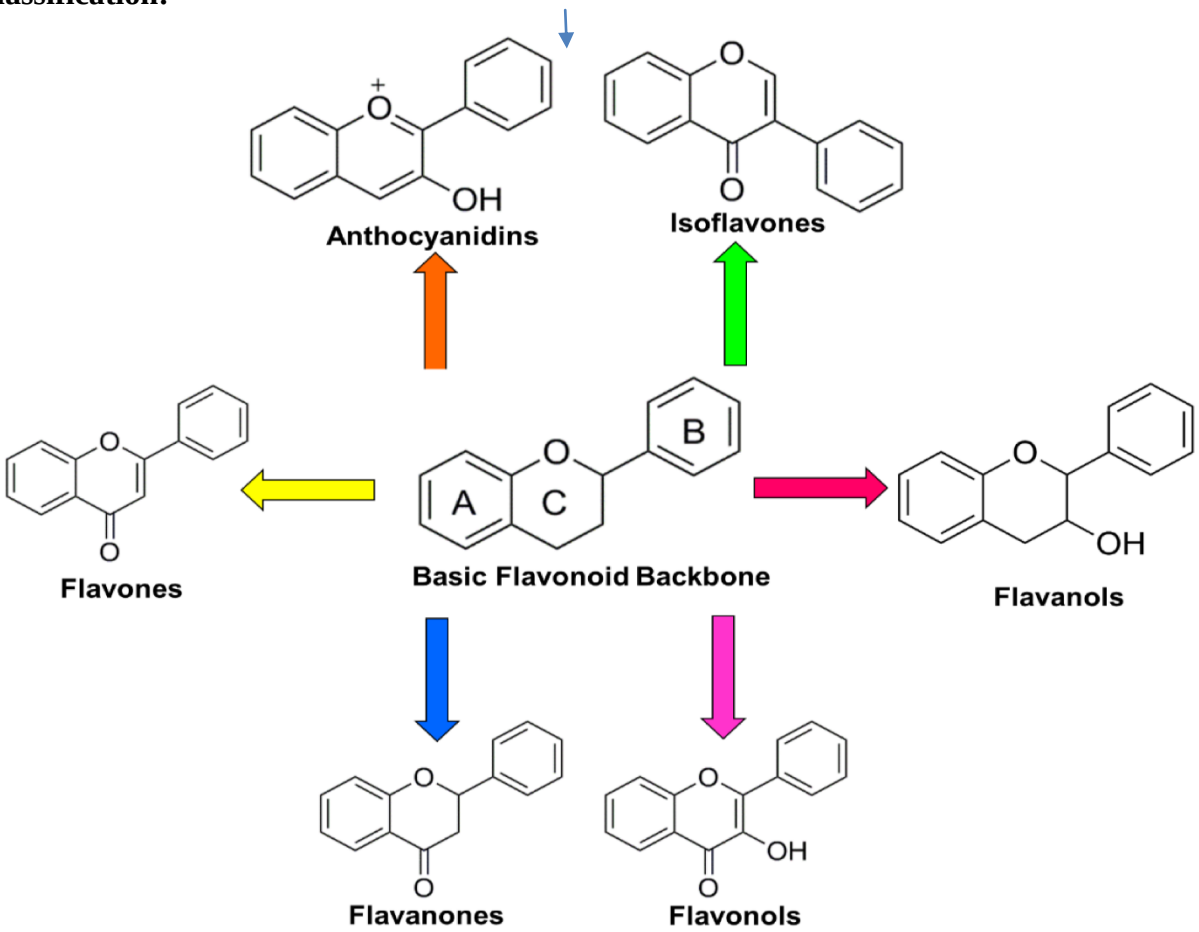
Flavonoids are a group of natural substances with variable phenolic structures which are present in fruits, vegetables, grains, bark, roots, stems, flowers, tea, and wine. These natural products are well known for their beneficial effects on health and efforts are being made to isolate the ingredients so-called flavonoids. Flavonoids have become an essential component in a wide range of nutraceutical, pharmacological, therapeutic, and cosmetic applications. They're thought to contain antiviral, anti-inflammatory, cardioprotective, anti-diabetic, anti-cancer, anti-aging, and other bioactive properties (Tian-yang Wang *et al.,* 2018). As a result, flavonoids, which are directly linked to human dietary elements, play a key role in disease prevention and have a wide range of health advantages. The several biological activities of flavonoids that have beneficial effects on human health are emphasized in this review.

Introduction:

Flavonoids are secondary metabolites that are very abundant in plants, fruits, and seeds, responsible for their color, fragrance, and flavor characteristics. In plants, flavonoids perform many functions, like regulating cell growth, attracting pollinators and insects, and protecting against biotic and abiotic stress (De Luna. *et al.* 2020,). Flavonoids are low molecular weight compounds (Fernandez *et al.,* 2006) bioactive polyphenols) that play an essential role in photosynthesizing cells. The original "flavonoid" research started in 1936, when Hungarian scientist Albert Szent-Gyorgi was uncovering a synergy between pure vitamin C and as yet unidentified cofactors from the peels of lemons, which he first called "citrin," and later it referred to as "vitamin P". Flavonoids have several biochemical and antioxidant effects associated with various diseases such as cancer, Alzheimer's disease (AD), atherosclerosis, etc. (Burak and Imen, 1999; Ovando *et al.,* 2009, Lee *et al.*, 2009). Flavonoids are associated with a broad spectrum of health-promoting effects and are an indispensable component in a variety of nutraceutical,

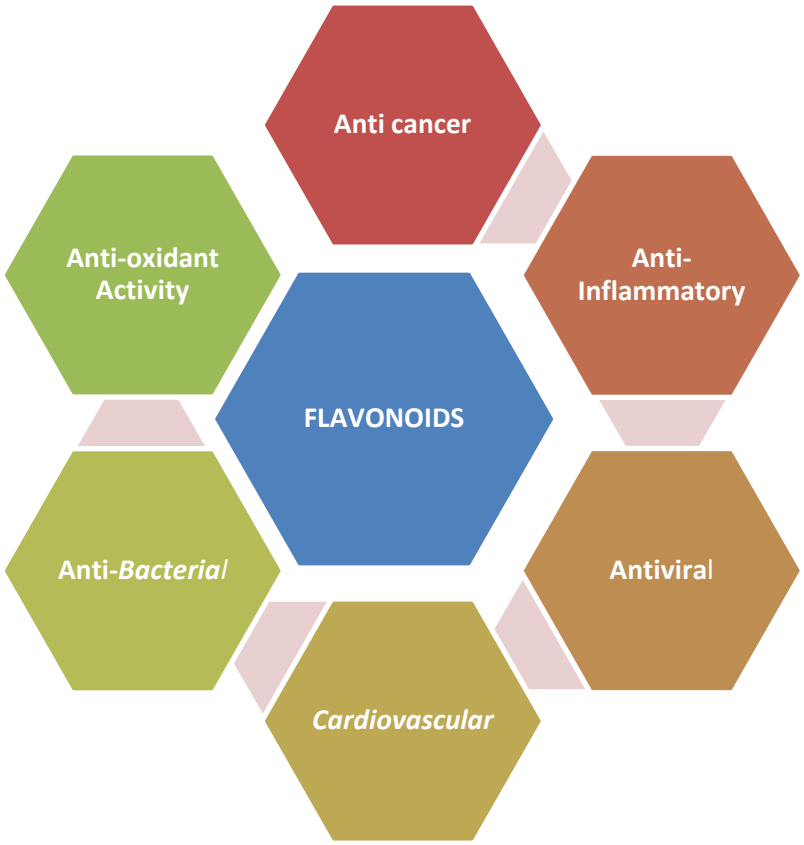
pharmaceutical, medicinal, and cosmetic applications. This is because of their potent anti-oxidative, anti-inflammatory, antimutagenic, antimicrobial, anti-carcinogenic, vascular activities, free radical scavenging abilities, and other medicinal properties coupled with their capacity to modulate essential cellular enzyme functions. The main aim of this review was to provide an overview of the research in the field of flavonoids. The potential physiological and antimicrobial actions of flavonoids are discussed. In the last part of this review article, the critical clinical applications of flavonoids in the human body system were discussed.

Classification:



Biological activity:

- Anti-oxidant Activity:
- Anti-Inflammatory Activity:
- Anti-*Bacterial* Activity:
- Antiviral Activity:
- Anti-Cancer Activity
- Cardiovascular protection



1. **Anti-oxidant Activity**

Antioxidants are molecules that protect cells in humans, animals, and plants from the harmful effects of free radicals. Flavonoids are the most well-known phytochemicals that act as antioxidants, inhibiting disease-causing agents. The arrangement of functional groups around the nuclear structure determines this action. Flavonoids have antioxidant properties that include suppressing ROS production by inhibiting enzymes, scavenging free radicals, and regulating antioxidant defenses. Flavonoids also protect biomembranes' lipids from damage caused by lipid peroxidation. As a result, flavonoids play an important role as antioxidants in the prevention of a variety of diseases caused by oxidative stress (Kelly *et al.*, 2002; Kukic *et al.*, 2006; Ramchoun *et al.*, 2009; Mishra *et al.*, 2013).

2. **Anti-bacterial Activity:**

Flavonoids are antibacterial compounds produced by plants in response to microbial infection. They are effective against a wide range of microorganisms. Apigenin and isoflavones have been shown to have antibacterial properties. Their ability to inactivate microbial adhesins, enzymes, and cell transport proteins may be connected to their antimicrobial mode of action. Microbial membranes may be damaged by lipophilic flavonoids (Cushineand Lamb, 2005).

3. Antiviral Activity:

Flavonoids, which are found in nature, have potent antiviral properties. They aid in the inhibition of different enzymes involved in the viral life cycle. In the selective suppression of HIV-1 and HIV-2, flavon-3-ol was found to be more effective than flavones and flavanones. Another flavonoid, baicalin, was discovered from Scutellariabaicalensis and has been shown to prevent HIV infections. Quercetin, Hesperetin, and Naringin have been seen to have anti-dengue virus properties (Gerdin and Srensso, 1983; Zandi *et al.,* 2011).

4. Anti-Cancer Activity:

Flavonoids are important in cancer prevention. They have an impact on carcinogenicity's initiation and promotion stages, as well as development and hormonal activity. Cell-cycle arrest, downregulation of mutant p53 protein, suppression of several cancer-triggering enzymes, and production of Ras proteins are among the additional methods of action. Many carcinogenesis situations are known to be reduced by flavonoids such as Flavonols, Isoflavone, and Quercetin (Davis and Mathew, 2000).

5. Anti-Inflammatory Activity:

Inflammation is a natural biological reaction to tissue damage, pathogen infection, and chemical irritants. Immune cells migrate from blood vessels and release mediators at the site of injury, which starts the process. The function of inflammatory cells to remove invading infections and restore the wounded immune system and inflammatory cell tissues follows this procedure. Anti-inflammatory properties are known to exist in Hesperidin, Luteolin, and Quercetin. They work by interfering with enzyme systems that are involved in the production of inflammatory processes. Phospho-di-esterases, which are involved in cell activation, are likewise inhibited by flavonoids.

6. Cardiovascular activity:

Atherosclerosis, coronary heart disease, arterial hypertension, and heart failure are all examples of cardiovascular illnesses. Oxidative stress is the primary cause of CVS illnesses and subsequent mortality. As antioxidants, flavonoids reduce oxidative stress and so contribute to all of the positive health impacts. Due to their hepto-protective activity, flavonoids are effective and safe in the treatment of hepatobiliary dysfunction and stomach problems (Tiwari, 2001; Spencer *et al.,* 2009).

7. Hepato-protective Activity:

Hepatic symptoms can be caused by a variety of chronic disorders, including diabetes and metabolic abnormalities. C3G therapy and Silymarin flavonoids have been shown to reduce hepatic lipid peroxidation and induce liver regeneration, respectively (Zhu *et al.,* 2012).

Conclusion:

The use of phytochemical substances, particularly flavonoids, to prevent and cure diseases is widely established. Flavonoids are found naturally in fruits and vegetables. Flavonoids are phytochemicals with a wide range of biological activities that benefit human health. In human diets, they are high in natural antioxidants. Flavonoids are excellent in neutralizing the detrimental effects of free radicals and so aid in the prevention of many diseases.They engage in a variety of cellular targets, including anti-oxidant and free-radical scavenger functions, as well as anti-inflammatory, antibacterial, antiviral, anti-aging, and, most importantly, anti-cancer capabilities. The benefits of flavonoids in human health are attributed to their dietary sources and several significant biological functions, according to this review. Their industrial applications go far beyond nutraceuticals and therapeutic candidate compounds.

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ADULTERATION OF FOOD

Omprakash S. Chavan

P.G., Department of Chemistry,

Badrinarayan Barwale College, Jalna-431213, Maharashtra, India

Affiliated to Dr. Babasaheb Ambedkar Marathwada University, Aurangabad, MS, India

*Corresponding author E-mail: omprakashschavan@gmail.com

Introduction:

Adulteration is a lawful term meaning that a food product flops to meet the legal ethics. One method of adulteration is an adding of another substance to a food element in order to increase the quantity of the food item in fresh form or prepared form, which outcomes in the loss of real quality of food item. These materials may be either existing food items or non-food items. Among meat as well as meat products several of the items used to adulterate are water or ice, carcasses, or carcasses of animals added than the animal meant to be used up.

Types of adulteration in food:

- **Intentional Adulteration:** Adding adulterants purposely to increase the food's weight and gain more income. E.g., mixing of stones, sand, chalk powder, etc.
- **Incidental Adulteration:** Occurs due to carelessness while handling food. e.g., residues of pesticides in grains.
- **Metallic Adulteration:** Inadvertently or intentionally adding metallic ingredients like lead from water and mercury from effluents.
- **Packaging Hazard:** Packing ingredients can also delay and mix with food components.

Reasons for food adulteration:

- Experienced as a part of business approach to fulfil trader's revenue motivation.
- No well-organized food law and lack of government ingenuities.
- Increased food ultimatum for a rapidly increasing population.
- Lack of awareness and attentiveness of proper food feeding by general public.
- To increase the amount of food production and sales under Food Uncertainty
- To make food well-dressed and ansynthetic of some other food this is in demand.

How to control food adulteration:

- Steps to taking careing while moving and stocking food products
- Steps to taking careing while handling food products.
- Steps to taking careing of while wrapping food products.

How to prevent food adulteration:

- On the manufacturing level, food adulteration can only be tested with firm and strict laws and government involvements and orders.
- General public should circumvent eating dark-coloured, garbage and other handled foods.
- Cleaning of fruits and vegetables systematically in running water previously they are used up.
- Check for drips in canned foods and authentication of seals in milk or oil pouches.
- Always checked and buy foods having an FSSAI-validated label, authorization number, list of constituents, factory-made date and its termination.

Food adulteration tests:

Adulteration done physically at household FSSAI has authenticated some common fast tests covering physical, chemical and sensory methods under Detect Adulteration with Rapid Test in numerous foodstuffs.

1. Adulteration of milk products and milk:

Some of the major adulterants in milk having serious dangerous chemical compounds like:

1. Detergents chemical
2. Formalin
3. Urea chemical
4. Caustic soda chemical
5. Boric acid chemical
6. Ammonium sulfate chemical
7. Sugars as sweetener
8. Salicylic acid aromatic compound
9. Hydrogen peroxide liquid.
10. Benzoic acid aromatic compounds
11. Melamine chemical

- Discovery of water in milk by checking the fluidity of milk sample, free running milk sample is adulteration of milk.
- Starch test is best test in which boil milk sample with iodine water blue colour shows adulteration is there.

2. Adulteration of oil and fats:

There are two main adulterations in comestible oils and fats namely

1) Adding and mixing cold pressedfats and oil with refined one

2) Changing of more costly oils and fats with inexpensive one

- Take small amount of yellow butter in tea spoon of sample oil, instant development of red colour shows presence of Tri-Ortho-Cresyl-Phosphate as adulteration component. (TOCP).

3. Adulteration in sugar and confectionary:

A very mostly used and common adulterants in sugar are,

1. A powdered plastic
2. Urea chemical
3. Washing soda a chemical
4. White chalk powder as Calcium carbonate
5. Direct Plastic crystals

- Take a glass of water, then add two tea spoon honey in it, wait for some time, if honey dispenses the it contain sugar as adulterants.

4. Adulteration in food grains and its products:

Contamination of food grains is the process of adding unwanted materials to the food grain, with parallel appearance, size and colour for buildingmore profits.

- In the adulteration of food grains and its products so many things are added by size, by shape, by colour, by weight, by physical appearance, etc.
- If coloured material is used as adulteration then food grains wash with water, colour will developed.
- If same sized and same coloured small rock is used as adulterant, and then mix the food grains with water, then rocky particles collect immediately at bottom.

5. Adulteration in Salt, spices and condiments:

Mostly many times, all types of spices alike turmeric powder, chilli powder, and other powdered spices have following types of adulteration.

1. A high percentage of residual pesticides.
2. Food colour
3. Added starch

4. Coloured saw dust

5. Brick powder, etc.

6. Iodised salt is repeatedly adulterated with non-iodised common salt, which can reasonto become unhealthy.

- Take small amount of asafoetida in stainless spoon and burn it on burner, pure burn like camphor and impure not in proper manner.
- Take some spoon of black pepper in a glass, then add clean water in it, if black pepper adulterate with papaya seed, seeds will float on surface of water.
- Take one tea spoon of turmeric powder in glass of water, natural turmeric powder will show yellow colour while settling down at bottom and adulterated one shows strong yellow colour.

6. Adulteration in fruits and vegetables:

Many fruits and vegetables are typically adulterated with a chemical dyes that is malachite green which is very dangerous to human body. That is carcinogenic. Some common adulterants in vegetables and fruits are

1. Oxytocin
2. Sachharin,
3. Wax,
4. Malachite green
4. Calcium carbide
5. Copper sulfate.
6. Ethylene gas
7. Cheap edible oil

- Take small piece of cotton, deep in water, then rub on leaves of vegetables, white cotton turn into green indicated adulteration of colour take place.

7. Adulteration in Beverages:

Adulterated alcoholic beverages islawful alcoholic goods that have been illegally tampered with water, some different flavours, some other impurities like methanol, etc.

- Add some coffee powder in a glass of water, observe it, if coffee powder adulterated with brisk particles, clay particles or chicory particles will settle at bottom.
- Take small quantity of coffee powder or tea leaves in a clean glass surface, take magnet and move it on coffee powder or tea leaves, iron particles will be seen on magnetsurfave hence exposure of adulteration.

8. Sensory evaluation quick tests:

- Synthetic milk provides bitter in taste, provides soapy feeling on rubbing if adulterated.
- Black pepper covered with mineral oil provides kerosene like smell.
- If urea is mixed with sugar, Rub sugar on palm and smell, urea presence will give ammonia smell.
- Normal taste of chapatti is sweetish and tasty while adulterated one is tasteless.

Advancements in checking food adulteration:

a. Electronic nose:

Electronic sensing replicate human senses by sensors and pattern- appreciation systems which are accomplished for documentation, evaluation, quantification, and additionaluses

including data storing and recovery used to distinguish aromas of food, diagnosescents and essences.

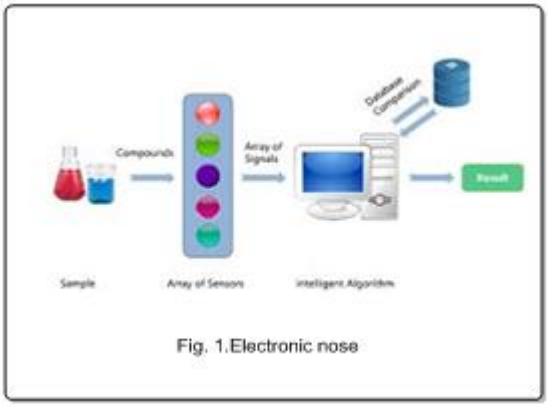

Fig. 1.Electronic nose

b. Optoelectronic sensing:

Optoelectronics is state that, it deals with the study of radiation, its discovery, construction and management which consist of x-rays, IR rays, Visible light rays, gamma rays, ultraviolet (UV). It act as detectors of light and transform it into signals and for analysis for computer processing. Anoptoelectronic sensing system consists of AVR microcontroller, optical sensor, LCD and keypad.

Fig. 2.Optoelectronic Sensing

c. IR spectroscopy:

Advanced IR spectroscopy is used to detect adulterants by very simple method.IR spectroscopy is also called as electronic tongue for adulteration of food.

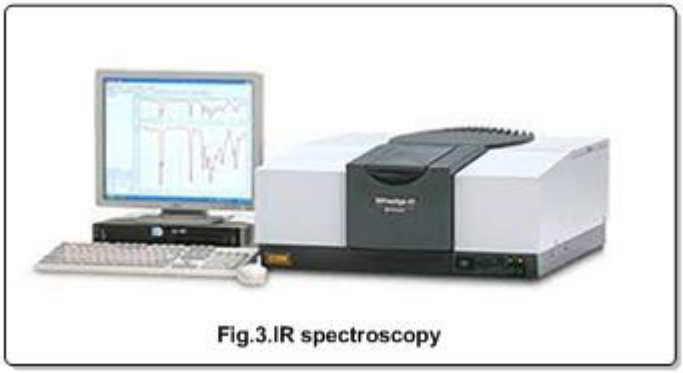

Fig.3.IR spectroscopy

d. Biosensors:

Biosensors are a small and very important device which is used for detection of impurities in bio samples like urea in milk.

Fig. 4. Biosensors

e. Surface Plasmon Resonance (SPR):

It is used for detect adulteration of very low concentrations.

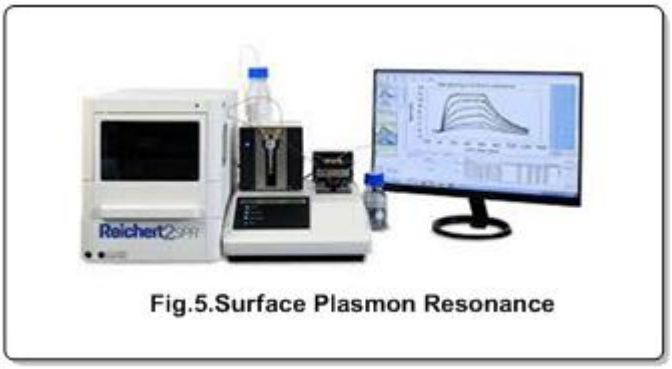

Fig.5.Surface Plasmon Resonance

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GREEN CORROSION INHIBITORS FOR MILD STEEL IN ACIDIC MEDIUM

Renu Singh* and Pinky Sisodia

Department of Chemistry,

Maharishi University of Information Technology, Lucknow

*Corresponding author E-mail: drrenu3110@gmail.com

Abstract:

Now a days due to increase in environmental pollution and increasing ecological awareness among all experts have led to the development of "eco-friendly" alternatives to lighten corrosion without using chemicals. In this paper work, literatures on many green corrosion inhibitors have been examined, and highlighted the primary trait in the field of corrosion. All eco-friendly extract serves as the chief substitute of the chemical corrosion inhibitors. Literature reveals that corrosion process of mild steel in acidic or other adverse environmental conditions can be inhibited or reduced by extracts of plant parts. All the reported plant extracts (natural corrosion inhibitors) were found usefulto inhibit the corrosion of mild steel in different media.

Keywords: Corrosion inhibitors, Eco-friendly, plant material, adverse condition

Introduction:

Corrosion is a natural phenomenon which converts metal into its more stable form .it is an oxidation process which involves deprivation of material or its useful properties by chemical interaction with its environment. On large scale, Carbon steel is the material of Chromium (Ch.) that is used in the fabrication of reaction vessels, storage tanks etc. and get corroded easily in the presence of acids. Hydrochloric acid solutions are generally used in several industrial processes like acid pickling of steel, chemical cleaning and processing, ore production and oil well acidification. Because of the general aggression of acid solutions on metals, corrosion inhibitors are commonly used to reduce the corrosive attack on metallic materials. Acid solutions are mostly used in the chemical industries to remove scales from metallic surfaces. These inhibitors are adsorbed on the surface of metal atom by depending on the structure. They forms complexes with metal ion onthe metal surface and form a protective coating on the metal surface and protecting them from corrosion in different media. Inhibition efficiency of these inhibitors in different media have been evaluated by employing various investigational techniques e.g. weight

loss method, electrochemical studies, Raman spectroscopy, potentiodynamic polarization, electrochemical impedance, polarization method, FTIR etc (1).

Among the various methods of corrosion control, use of Green corrosion inhibitors is very popular due to the ease of application. Plant extracts contains several organic compounds with heteroatom such as N, O, S and P, they are adsorbed directly on themetallic surface through polar atoms and thereby forming the protective layer on metal surface.Plant extracts plays important role due to environmentally acceptable, non-toxic, easily available and are also renewable. This paper reviews and discusses states the use of different types of eco-friendly green corrosion inhibitors to control the corrosion of mild steel in acidic media. Corrosion control of metals and their alloys is essential and significant at an environmentally imperative matter. Extracts of plant material serves as a superior alternativeof hazardous organic and inorganic corrosion inhibitors. So many plant extracts have shown to be highly efficient green corrosion inhibitors both in acidic and alkaline medium (2).

Conclusions:

The overall summarisation concluded that the naturally occurring plant extracts are easily and readily available, cheap, renewable and are both eco-friendly and ecologically acceptable. It is required to minimize and control metallic corrosion which is a major industrial and domestic problem. Green Corrosion Inhibitors are found to be very effective and can plays important role over toxic corrosion inhibitors. The efficiency of corrosion inhibitors depends not only on the kind of the environment, the nature of the metallic surface, but also on the structure of thecorrosion inhibitor itselfthat includes the number of adsorption active centres in the molecule, their molecular size, charge density, mode of adsorptionand the projected area of the inhibitor on the metallic surface. From the experimental studies it can be concluded that the main mechanism of corrosion inhibition follows the different adsorption isotherms and their adsorption depends on the physical and chemical properties of the metallic surface. Studies also revealed that the corrosion inhibition of mild steel in acidic medium is concentration dependent and the inhibition efficiency increases with increase in the concentration of inhibitors. The corrosion inhibition of mild steel occurs through adsorption of inhibitors on the corroding metal surface. These adsorption studies follow Langmuir, Freundlich, Temkin adsorption isotherm or thermodynamic kinetic model. The non-toxic and eco-friendly green corrosion inhibitors can therefore be considered as the most essential and beneficial for men and environmentboth. Thus it may be concluded that the eco-friendly green corrosion inhibitors obtained from plant extracts have a broad space and can be used as a replacement of hazardous and toxic inorganic and organic chemicals.

Eco-friendly green corrosion inhibitors to controlcorrosion of mild steel:

Table 1: Various plant extracts that have been used as a corrosion inhibitor for mild steel in acidic medium

Sr. No	Medium	Inhibitors	Technique	Findings	Reference
1.	1.0 M H_2SO_4	*Carica papaya*	Gravimetric and Gasometric techniques	Langmuir and Temkin adsorption isotherms.	3
2.	1 M HCl	*eugenol*	weight loss measurements, electrochemical polarisation and EIS methods	Langmuir adsorption isotherm.	4
3.	1 M HCl	*fenugreek*	weight loss, polarisation and EIS measurements	Gravimetric measurements Polarisation measurements	5
4.	1% NaCl	*Cinnamon Extract*	Weight Loss Method, Inhibition, Surface Study, Open Circuit Potential, Tafel Plot	Open Circuit Potential, Tafel Plot Freundlich and Frumkin Langmuir adsorption isotherm	6
5.	2 M HCl	*Aningeria Robusta*	chemical adsorption	Langmuir adsorption isotherm	7
6.	1M HCl	*Prosopis cineraria*	Weight loss method	Mass Loss Method	8
7.	1MHCl	*Atropa belladonna*	Potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques	a mixed-type	9

8.	1 M HCl	*Ananas comosus*	kinetic and thermodynamic	Langmuir adsorption	10
9.	2 M HCl	Antibacterial drugs	hydrogen evolution, weight loss, and Potentiostatic polarization techniques	Langmuir adsorption isotherm	11
10.	2 M H_2SO_4	*Exudate gum from Pachylobus*	thermometric methods	Temkin adsorption	12
11.	1H_2SO_4	*Combretum bractesum*	Frumkin adsorption isotherm	gravimetric and hydrogen evolution	13
12.	1N HCl	*Emblica officinalis (Indian Gooseberry)*	weight loss measurements	e Langmuir, Temkin, Freundlich and Flory Huggins adsorption isotherms.	14
13.	1MHCl	*Pineapple leaves extract*	Weight loss and hydrogen evolution methods	Langmuir adsorption isotherm	15
14.	1MHCl and 0.5 M H_2SO_4	*Murraya koenigii*	Weight loss, electrochemical impedance spectroscopy (EIS), linear polarization and potentiodynamic polarization techniques.	Langmuir adsorption isotherm.	16
15.	1 M HCl	*Azadirachta indica*	EIS, LPR, and weight loss	mixed type of inhibitors	17
16.	5 M H_2SO_4	*Calotropis procera*	Weight loss, Electrochemical, SEM and UV methods	Temkin adsorption isotherm	18
17.	n 0.1M solutions of NaCl and NaOH	Lawsonia extract	Langmuir adsorption isotherm.	mixed inhibitor	19

18.	2 M HCl	*olive leaves (Oleaeuropaea L.)*	weight loss measurements, Tafel polarization, and cyclic voltammetry	Langmuir adsorption isotherm.	20
19.	1 N HCl	*Eclipta Alba by lupine extract*	weight loss, potentiodynamic polarization and impedance methods	mixed type inhibitor	21
20.	1 M HCl and H_2SO_4	*Solanum tuberosum*	Potentiodynamic polarization, Electrochemical Impedance Spectroscopy (EIS) and SEM techniques	Temkin adsorption isotherm	22
21.	$1MH_2SO_4$	*Nauclealati folia*	gasometric and gravimetric techniques.	Weight loss	23
22.	1 MHCl	*Khillah extract (Ammivisnaga)*	weight loss measurements as well as potentiostatic technique		24
23.	1M phosphoric acid	*Sidarhom bifolia*	Weight loss measurements, polarization and electrochemical impedance spectral studies.	Langmuir and Temkin	25
24.	1 MHCl	*Mentha pulegium*	Weight loss measurements, electrochemical polarisation and EIS methods.		26
25.	1 MHCl	*Zenthoxy lumalatum*	Weight loss and electrochemical impedance spectroscopy (EIS).	SEM, XPS and FT-IR	27
26.	1M NaCl	*Ricinus communis (Castor-oil plant)*	electrochemical polarization and impedance measurements	weight loss	28

27.	H_2SO_4	*Centella asiatica (Vallarai)*	The gravimetric and hydrogen evolution	Frumkin adsorption	29
28.	5M H_2SO_4	*Azadirachta indica*	Weight loss and gasometric techniques.	. Freundlich adsorption isotherm.	17
29.	1 MHCl	*Oxandra asbeckii*	potentiodynamic polarization and electrochemical impedance spectroscopy (EIS)	Mixed-type inhibitor.	30
30.	1 M HCl	*Annona squamosa*	Potentiodynamic polarization and AC impedance methods	mixed-type inhibitor	31
31.	1 M HCl	*Karanj (Pongamia pinnata)*	Weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization, and linear polarization techniques.	mixed-type inhibitor	31
32.	1 M HCl	*shahjan (Moringa oleifera)*	Weight loss, electrochemical impedance spectroscopy (EIS), linear polarization, and potentiodynamic polarization techniques (Tafel).	Langmuir adsorption isotherm.	31
33.	1 M HCl	*Kuchla (Strychnosnux vomica)*	Weight loss, electrochemical impedance spectroscopy, potentiodynamic polarization and linear polarization techniques.	weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS)	32

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USE OF ESSENTIAL OILS IN INSECT PEST MANAGEMENT

Vinod Kumar Dubey*[1] and Kavita Jain[2]

[1]Department of Entomology,

Post Graduate College of Agriculture,

Dr. Rajendra Prasad Central Agricultural University,

Pusa, Samastipur, (Bihar)-848125

[2]Division of Nematology,

Indian Agricultural Research Institute, Pusa, New Delhi-110012

*Corresponding author E-mail: vinodkumardubey42@gmail.com

Introduction:

The environmental problems caused by over use of pesticides have been the matter of concern for both scientists and public in recent years. It has been estimated that about 2.5 million tons of pesticides are used on crops each year and the worldwide damage caused by pesticides reaches $100 billion annually. The reasons for this are: (1) the high toxicity and non-biodegradable properties of pesticides and (2) the residues in soil, water resources and crops that affect public health. Thus, on the one hand, one needs to search the new highly selective and biodegradable pesticides to solve the problem of long term toxicity to mammals and, on the other hand, one must study the environmental friendly pesticides and develop techniques that can be used to reduce pesticide use while maintaining crop yields. Natural products are an excellent alternative to synthetic pesticides as a means to reduce negative impacts to human health and the environment. The move toward green chemistry processes and the continuing need for developing new crop protection tools with novel modes of action makes discovery and commercialization of natural products as green pesticides an attractive and profitable pursuit that is commanding attention. The concept of "Green Pesticides" refers to all types of nature-oriented and beneficial pest control materials that can contribute to reduce the pest population and increase food production. They are safe and ecofriendly. They are more compatible with the environmental components than synthetic pesticides (Isman and Machial, 2006).

Many plant essential oils show a broad spectrum of activity against pest insects and plant pathogenic fungi ranging from insecticidal, antifeedant, repellent, oviposition deterrent, growth regulatory and antivector activities. These oils also have a long tradition of use in the protection of stored products. Recent investigations indicate that some chemical constituents of these oils

interfere with the octopaminergic nervous system in insects. As this target site is not shared with mammals, most essential oil chemicals are relatively non-toxic to mammals and fish in toxicological tests, and meet the criteria for "reduced risk" pesticides. Some of these oils and their constituent chemicals are widely used as flavoring agents in foods and beverages and are even exempt from pesticide registration. This special regulatory status combined with the wide availability of essential oils from the flavor and fragrance industries, has made it possible to fasttrack commercialization of essential oil-based pesticides. Though well received by consumers for use against home and garden pests, these "green pesticides" can also prove effective in agricultural situations, particularly for organic food production. Further, while resistance development continues to be an issue for many synthetic pesticides, it is likely that resistance will develop more slowly to essential-oil-based pesticides owing to the complex mixtures of constituents that characterize many of these oils. Ultimately, it is in developing countries which are rich in endemic plant biodiversity that these pesticides may ultimately have their greatest impact in future integrated pest management (IPM) programmes due to their safety to non-target organisms and the environment.

Essential oils are the highly volatile oils with strong aromatic components and these are the by-products of plant metabolism and commonly referred as a volatile plant secondary metabolites extracted from various plant parts *viz*., leaves, stems, seeds, flowers, fruits, roots, rhizomes and wood (Koul *et al.*, 2008). Essential oils are known to present in 17,500 aromatic species of higher plants belonging to a few families, including the Myrtaceae, Lauraceae, Laminaceae and Asteraceae. Many plant essential oils show a broad spectrum of activity against insect pest and plant pathogenic fungi ranging from insecticidal, antifeedant, repellent, oviposition deterrent, fumigant and growth regulatory activities (Roger *et al.*, 2012). Many essential oils are also acutely toxic to a variety of insects and can impose more chronic, sub lethal effects on growth. As a result of their highly volatile nature, essential oils are not persistent in the environment and are less likely to leave residues on food products. These favorable properties of essential oils suggest that products based on them may be viable options as a part of IPM.

Essential oils used in pest management

Sr. No	Oil Name	Taxonomy	Family
1.	Cedar wood oil	*Juniperus virginiana* L	Cupressaceae
2.	Cinnamon oil	*Cinnamomum zeylanicum*	Lauraceae
3.	Citronella oil	*Cymbopogon nardus*	Poaceae
4.	Niaouli oil	*Melaleuca viridiflora*	Myrtaceae
5.	Eucalyptus oil (1-8-cineole)	*Eucalyptus globulus*	Myrtaceae
6.	Garlic oil	*Allium sativum*	Alliaceae
7.	Lavender oil	*Lavandula angustifolium*	Rutaceae
8.	Lemon grass oil	*Cymbopogon citratus*	Poaceae
9.	Majoram oil	*Thymus mastichina*	Lamiaceae
10.	Patchouli oil	*Pogostemon cablin*	Lamiaceae
11.	Pennyroyol oil	*Mentha pulegium*	Lamiaceae
12.	Pepparmint oil	*Mentha piperita*	Lamiaceae
13.	Rosemary oil	*Rosmarinus officinalis*	Lamiaceae
14.	Thyme oil	*Thymus vulgaris*	Lamiaceae
15.	Cineole (Mugwort oil), alpha-Pinene	*Artemisia vulgaris,*	Asteraceae
16.	α-bisabolol	*Chamomile recutita (daisy)*	Asteraceae
19.	Asarone	*Acorus calamus (sweet flag)*	Acoraceae
20.	Dill oil	*Anthema sowa*	Asteraceae
21.	Citronellol, Geraniol	*Pelargonium spp (Geranium)*	Geraniaceae
22.	Anethole	*Pimpinella anisum and Foeniculum vulgare (fennel)*	Apiaceae
23.	Ajwain oil	*Trachyspermum spp*	Apiceae

Essential oil constituents and their efficacy

As mentioned above essential oils are complex mixtures of natural organic compounds which are predominantly composed of terpenes (hydrocarbons) such as myrecene, pinene, terpinene, limonene, *p*cymene, α- and β- phellandrene etc.; and terpenoids (oxygen containing hydrocarbons) such as acyclic monoterpene alcohols (geraniol, linalool), monocyclic alcohols (menthol, 4-carvomenthenol, terpineol, carveol, borneol,), aliphatic aldehydes (citral, citronellal,

Active Constituent	Plant
Eugenol	*Eugenia cryophyllus*
1,8- cineole	*Eucalyptus globules*
Citronellal	*Cymbopogonnardus*
Pulegone	*Menthapulegium*
Thymol and carvacrol	*Thymus vulgaris*
α-phellandrene	*Curcuma longa*

Aromatic phenols (carvacrol, thymol, safrol, eugenol), bicyclic alcohol (verbenol), monocyclic ketones (menthone, pulegone, carvone), bicyclic monoterpenic ketones (thujone, verbenone, fenchone), acids (citronellic acid, cinnamic acid) and esters (linalyl acetate). Some essential oils may also contain oxides (1,8- cineole), sulphur containing constituents, methyl anthranilate, coumarins, etc. Zingiberene, curcumene, farnesol, sesquiphellandrene, termerone, nerolidol, etc. are examples of sesquiterpenes (C_{15}) isolated from essential oils. Mono- and sesquiterpenoidal essential oil constituents are formed by the condensation of isopentenyl pyrophosphate units. Diterpenes usually do not occur in essential oils but are sometimes encountered as by-products. Chemical structures of some of the essential oil constituents are given in Fig. 1 and many among them possess potent biological activity and are responsible for the bitter taste and toxic properties.

Different methods of extraction of essential oils

- Hydro-distillation
- Steam distillation
- Dry distillation
- Mechanical cold pressing

Among these methods steam distillation is the popular method. Steam distillation process it separates a relatively clean secondary metabolite fraction from plants, including mainly low-molecular-weight volatile phytochemicals, terpenes and phenolic origin.

Mode of action of essential oils/components

1. Penetrants - disruption of lipid bilayers in cells

2. Good synergists:

e.g: Piperamides have a remarkable synergism when combined with pyrethrin.

3. **Inhibitors of insect P450 cytochromes**

eg: i. Dillapiole in dill oil (*Anthema sowa),*

ii. Piperamides *from Piper* spp

4. **Neurotoxic:** several monoterpenes

Thymol acts on GABA receptors

5. **Eugenol** - **octopaminergic system** by activating receptor for octopamine, which is a neuromodulator.

6. **Specialized odorant binding proteins (OBPs)** –

Volatile monoterpenes.

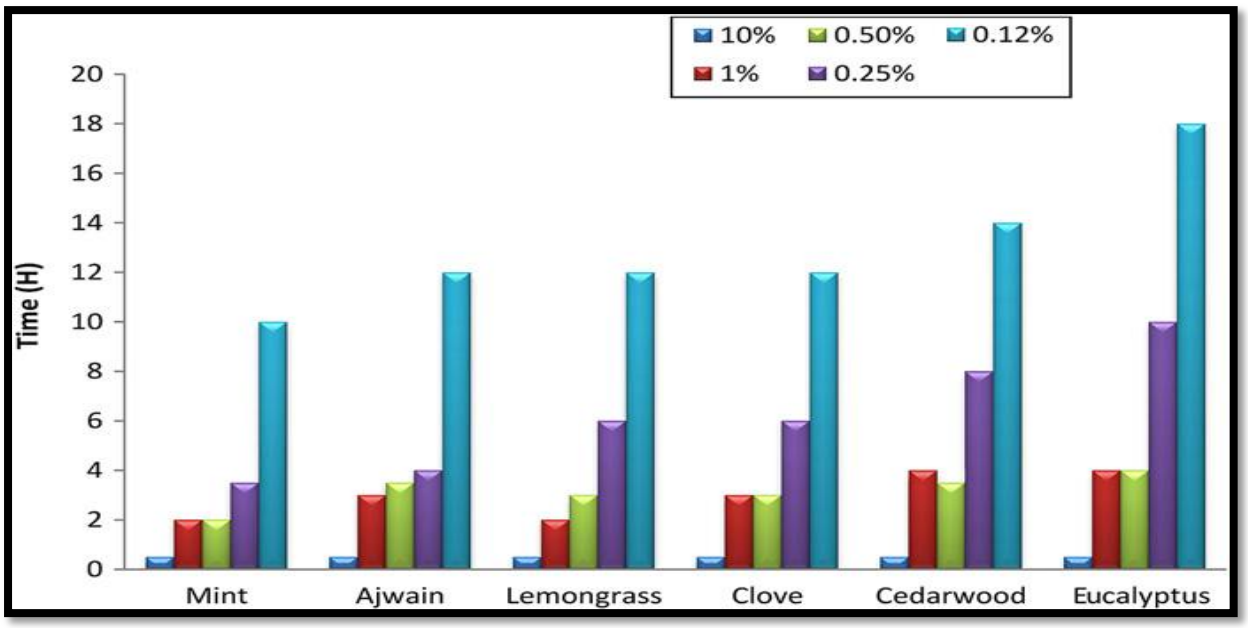
Eg: *Manduca sexta* - **OBP** preferentially interacts with floral aromas and green plant odours such as geranial and limonene.

Insecticides and growth inhibitors

Evidently, the mode of action studies on natural plant fumigants in insects has largely focused on monoterpenoids. It is important to study the mode of action of other compounds with appreciable fumigant action such as methyl disulphide, methyl thiocyanate, methyl allyldisulphide and thiosulfinates.

Sr. No.	Compound	Insect pest	LD_{50} Dose(µg/insect)
1.	Citronella oil	*S. litura*, *M. domestica*	66.0–111.2
2.	d-Limonene	*M. domestica*, *S. Litura*, some stored grain pests and cockroaches	50–273.7
3.	Thymol	*M.domestica* and S. litura	25.4–29.0
4.	Eugenol	*Spodopteralitura*, *Sitophilus granaries*	2.5–157.6

Mortality rates of *O. obesus*workers with different concentrations of selected essential oils

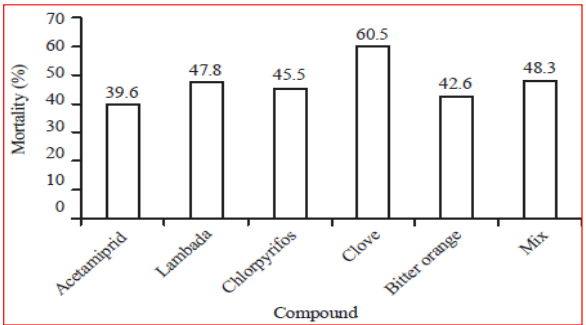


Aditi and his co-workers they conducted experiment on Percentage mortality of Termite workers time with 0.12% oil.

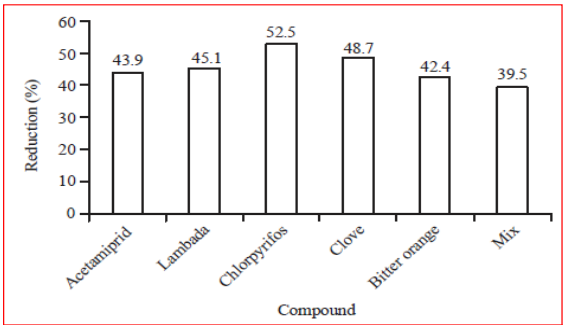
The biopesticidal potential of six plant-derived essential oils (mint [Menthaarvensis], ajwain [Carumcapticum], lemongrass [Cymbopogon citrates], clove [Eugenia caryophyllata], cedarwood [Cedrusdeodara], and eucalyptus [Eucalyptus globulas]) was evaluated against *Odontotermesobesus* (termites), *Fusariumoxysporum* (plant pathogenic fungi), and *Meloidogyne incognita* (nematodes). In the case of termites, a "no-choice" bioassay revealed that the mint oil gave the best results (100% mortality in 30 min with 10% oil and in 10 h with 0.12% oil) followed by the lemongrass and ajwain oils.

Ibrahim *et al.* (2016) evaluated the three insecticides, acetamiprid, lambda-cyhalothrin chloropyriphos and two natural oils, clove, bitter orange and mixture of both (1:1) in depress infestation of tomato plant by *Liriomyza trifolli, Bemisia argentifolii* and *Tuta absoluta* were carried out under semi field conditions. According to general mean of mortality, clove oil had the highest (60.5%) effect against *L. trifolli* followed by mixed oil (48.3%), while acetamiprid had the lowest toxicity effect with 39.6% of reduced mortality. Also, data clarified that lambda and mixed oil (clove and bitter orange oils 1:1) were the highest effective oils against eggs of *B. argentifolii*, both caused 85.3 reductions in eggs count, respectively, while acetamiprid was the lowest (50.9%). Clove gave satisfactory results against *L. trifolli, B. argentifolii* and *T.absoluta*, respectively.

Effects of some insecticides and natural volatile oils on *Leaf minors*



General mean of mortality percent (%) of tested compounds on *L. trifolli*



General mean of reduction percent (%) of tunnels count/20 tomato leaflets infested by *L. trifolli*

Treatments	Reduction infestation (%)	Real mortality (%)
Acetamiprid	50.0	88.95
Lambada	45.8	29.70
Chlorpyrifos	58.3	77.30
Clove	62.5	87.30
Bitter orange	58.3	26.30
Mix	33.3	70.50
Control	..	-

on *Tuta absoluta*

Ibrahim *et al.* (2016)

Fumigants

Monoterpenes being volatile are more useful as insect fumigants. Several studies have been undertaken in the past to explore the potential of essential oils and their constituents as insect fumigants. Pulegone, linalool and limonene are known effective fumigants against rice weevil, *Sitophilus oryzae*. While *Menthacitrata* oil containing linalool and linalyl acetate exhibit significant fumigant toxicity to these rice weevils (Singh *et al.*, 1989), *l*-carvone has been reported to cause 24 times more fumigant toxicity than its contact toxicity to lesser grain borer, *Rhizoperthadomestica* (Tripathi *et al.*, 2003). Carvone was similarly effective as adulticide while menthol was most effective as fumigant against *T. castaneum*and *C. maculatus.* 1,8-cineole on the other hand exhibits both contact and fumigant toxicity when tested against *T. castaneum* (Tripathi *et al.*, 2001). The adults were more susceptible than the larvae to both contact and fumigant toxicity. Number of compounds has been evaluated as fumigants against *Musca domestica*and *T. castaneum.* LC_{50} (µg/l) values have been determined for carvacrol, carveol, geraniol, linalool, menthol, terpineol, thymol, verbenol, carvones, fenchone, menthone, pulegone, thujone, verbenone, cinnamaldehyde, citral, citronellal, and cinnamic acid (Rice and Coats, 1994). These studies reveal that ketones were more effective as fumigants.

Sr. No.	Compound	Insect pest	LD_{50} Dose	Reference
1.	Anethole	*T. castaneum*	20 µl/l -80 µl/l concentration	Koul*et al.*, 2007
2.	Anethole + 1,8-cineole (1:1)	*T. castaneum*	50µl/l concentration	Koul*et al.*, 2007
3.	Cymbopogon oil	*C. maculatus*	33.3 µl/l concentration	Ketoh*et al.*,2005
4.	1,8-cineole	*Sitophilus oryzae*	19.0–30.6 µl/l concentration	Lee *et al.*, 2004

Efficacy of essential oils and formic acid against varroa mite, *V. destructor* based on per cent mortality in *A. mellifera* colonies.

Treatment	Oils	Per cent mite mortality			
		1st week after treatment	2nd week after treatment	3rd week after treatment	Mean
T_1	Tulsi oil	71.16 (25.12)*	69.23 (27..40)	63.78 (24.09)	68.56
T_2	Garlic oil	76.73 (28.07)	76.00 (27.53)	72.36 (26.57)	75.03
T_3	Turmeric oil	72.72 (26.23)	71.87 (25.67)	67.06 (26.28)	70.55
T_4	Ajwain oil	55.51 (23.74)	61.72 (23.68)	53.33 (22.43)	56.85
T_5	Cinnamon oil	70.63 (27.47)	68.14 (26.79)	56.25 (24.04)	65.00
T_6	Clove oil	71.85 (26.46)	70.37 (25.89)	65.58 (25.67)	69.26
T_7	Formic acid	75.82 (27.72)	75.59 (27.74)	67.43 (26.41)	72.94
T_8	Control	0.00 (0.00)	0.00 (0.00)	0.00 (0.00)	0.00
SEM±		**2.73 (1.93)**	**2.77 (1.10)**	**1.52 (1.13)**	**1.43**
CD at 5%		**20.82 (18.85)**	**14.00 (13.36)**	**18.57 (16.45)**	**15.09**

The results revealed among seven treatments applied for varroa mite control, Garlic oil (T2) treatment gave significantly superior results in reducing the varroa mite population up to three weeks with an overall mean value of 75.03 per cent followed by formic acid giving 72.94 per cent mite mortality.

Hyssop (*Hyssopus offcinalis*), majoram (*Origanum majorana*) and *Thymus zygis* essential oils showed strong fumigant toxicity against S. *oryzae* adults at 25 mg/L air concentration.

Trans-anethole, thymol, 1,8-cineole, carvacrol, terpineol, and linalool have been evaluated as fumigants against *T. castaneum*. Only compound to show significant effect against this insect species was *trans*anethole and red flour beetles seemed to be least susceptible to most of the other compounds up to 300 µl/l fumigation. Anethole has shown significant effect on population from 20 µl/l concentration (66% reduction in population), which touched to 98% at 80 µl/l level and beyond this there was absolute control of population generation. For improving the mortality effect of anethole, minimum heat treatment (45°C) device was used that enhanced the toxicity of adults by 2-fold at 50.0 µl/l and 100.0 µl/5l treatment, respectively. Among various combinations of compounds used anethole combined with 1,8-cineole (1:1) was the best. This combination reduced the population by 100% at 50µl/l concentration and at the same time was toxic to adults as well. As *T. castaneum* was resistant to most of the compounds, a workable gelatin capsule formulation (IBRCTACT) based on combination of four compounds has been developed, which reduced the progeny by 100%. A significant observation has been that when treatment was continued for larvae in 5-litre jars (with feeding medium) and insects were allowed to complete life cycle under treated conditions the freshly emerged adults coming to the surface of the feeding medium were dead within 12 h. This suggests that freshly emerged adults were highly susceptible to the treatment of anethole or IBRC-TACT and could not withstand the effect of compounds. One of the plausible explanations for such an effect could be the interference during the scelortization immediately after the emergence from pupae, which ultimately leads to the death of beetles within 12 h of their emergence (Koul*et al*., 2007).

The fumigant effects of ***Ocimum gratissimum* L. oil** and its constituents, **b-(Z)-ocimene and eugenol,** were evaluated against adults of

- *Sitophilus oryzae* (L.),
- *Tribolium castaneum*(Herbst),
- *Oryzaephilus surinamensis* (L.),
- *Rhyzopertha dominica* (F.),
- *Callosobruchus chinensis* (L.)

Antifeedants

Antifeedant chemicals may be defined as being either repellent without making direct contact to insect, or suppressant or deterrent from feeding once contact has been made with insects. Essential oil constituents such as thymol, citronellal and α-terpineol are effective as

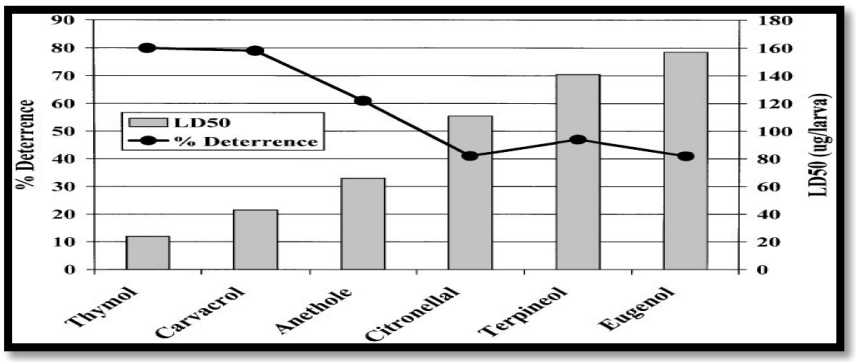
feeding deterrent against tobacco cutworm, *S. litura* and synergism or additive effects of combination of monoterpenoid.

Sr. No.	Compound	Insect pest	LD_{50} Dose (µg/larva)
1.	Linalool	*S.litura*	85.5
2.	1,8-cineole	*S.litura*	126.6
3.	Thymol + anethole*synergized the effects* of linalool, combined in 1:1 ratio	*S.litura*	18
4.	Majoram and rosemary oil	Onion Thrips *Thripstabaci*	0.1–1.0 *
5.	*Citronella oil and Callistemon* oil	Onion Thrips *Thripstabaci*	10 *
6.	Mugwort oil	*S. obliqua* *S. litura*	0.4 **

(Source: *Koschier *et al*., 2001; ** Chowdhury *et al*., 2000)

Essential oils have been reported against *S. litura* larvae (Hummelbrunner and Isman, 2001). Bioefficacy of *Eucalyptuscamaldulensis* var. *obtusa* and *Luvangascandans* essential oils has also been determined against *S. litura* larvae. Biogenically related monoterpenoids, the 1,8-cineole from *Eucalyptuscamaldulensis* var. *obtusa* and linalool from *Luvangascandans* species were found to be most active isolates from these plants via topical application. Linalool was more active (LD_{50} = 85.5 µg/ larva) than 1,8-cineole (LD_{50} = 126.6 µg/larva). Various known monoterpenoids have been used as binary mixtures and tested for synergy, using toxicity and feeding inhibition parameters. The data suggests that thymol and *trans*-anethole synergized the effects of linalool (at 18 µg/larva dose, combined in 1:1 ratio) but thymol with 1,8-cineole exhibited only additive effect and so was the case with terpineol and linalool combination. A definite synergism was also observed in case of isolated compounds from two different plant species, i.e. linalool with 1,8cineole (Singh *et al.*, 2008).

Feeding deterrence of oils to the tobacco cutworm *S. litura* (Isman *et al.*, 2000)



Toxicity of selected essential oils monoterpines and phenols for four species of insects and one species of mites

Species	LC 50 or LD 50			
	Eugenol	Carvocral	Alpha terpeniol	Trpinen 4-ol
Spodoptera litura	157.6	427	141.3	130.4
Drosophila melonogaster	46	48	17.4	17.7
Musca domestica	72	92	173	79
Diabrotica tingifera	12	NT	112	90
Tetranychus urticae	219	629	NT	96

Sr.No.	Crop	Compound	Insect pest	LD_{50} Dose
1.	*Luvanga scandans*	Linalool	S. litura	85.5 µg/larva
2.	*Eucalyptus*	1,8-cineole	S. litura	126.6 µg/larva
3.	*Thymus vulgaris*	Thymol + anethole synergized the effects of linalool, combined in 1:1 ratio	S. litura	18 µg/larva dose

Effect of Aqueous extracts of selected plant species on hatchabilty of eggs of *S. litura*

Treat. No	Treatment	Mean per cent eggs unhatched
T_1	7.5 per cent ratntulas leaf extract (RTLE)	45.00 (42.11)*
T_2	10.0 per cent ratntulas leaf extract (RTLE)	55.00 (47.88)
T_3	7.5 per cent Kumbha fruit extract (KFE)	35.00 (36.22)
T_4	**10.0 per cent Kumbha fruit extract (KFE)**	**65.00 (53.77)**
T_5	7.5 per cent Bhamrud leaf extract (BLE)	30.00 (32.89)
T_6	10.0 per cent Bhamrud leaf extract (BLE)	35.00 (36.22)
T_7	7.5 per cent Ranmodi leaf extract (RLE)	30.00 (33.21)
T_8	10.0 per cent Ranmodi leaf extract (RLE)	45.00 (42.11)
T_9	7.5 per cent Datpadi leaf extract (DPLE)	25.00 (29.88)
T_{10}	10.0 per cent Datpadi leaf extract (DPLE)	30.00 (33.21)

T_{11}	7.5 per cent Davana leaf extract (DLE)	15.00 (22.49)
T_{12}	10.0 per cent Davana leaf extract (DLE)	25.00 (29.88)
T_{13}	5.0 per cent Davanaleaf extract (DLE)	35.00 (36.22)
T_{14}	7.5 per cent neem seed kernal extract (NSKE)	40.00 (39.23)
T_{15}	**10.0 per cent neem seed kernal extract (NSKE)**	**65.00 (53.77)**
T_{16}	0.05 per cent endosulfan 35 EC	45.00 (42.11)
T_{17}	Conrol (Water Spray)	15.00 (22.49)
	S. E .±	3.20
	C. D. at 5 per cent	9.54

Dr.BSKKV Dapoli Mane (2006) evaluated.

Conclusion:

Certain plant essential oils and/or their constituents have a broad spectrum of activity against insect and mite pests, plant pathogenic and other fungi, and nematodes. As such, they have considerable potential as crop protectants and for pest management in other situations (e.g. urban pest control). Current information indicates that they are safe to the user and the environment, with few quali$_{fi}$cations. As a cautionary note, the essential oils that are most e$_{ffi}$cacious against pests are often the most phytotoxic; this latter property requires serious attention when formulating products for agricultural and landscape use. Like other alternative pest management products, essential oil-based pesticides will not be a panacea for crop protection, but there should be substantial market niches, particularly where there is a premium on worker safety and environmental protection, in which these types of products will $_{fi}$nd wide acceptance among growers.

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PEG400: AN ALTERNATE GREEN REACTION SOLVENT FOR SYNTHESIS OF HETEROCYCLES

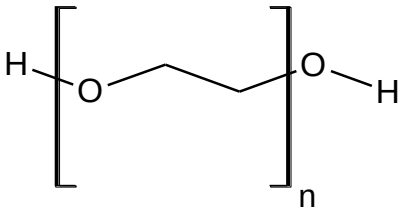
Shaikh Abdul Baseer

Department of Chemistry

Sir Sayyed College of Arts, Commerce and Science,

Aurangabad, Maharashtra India

Corresponding author E-mail: baseershaikh@gmail.com



Applications of polyethylene glycol PEG-400 as an efficient and green reaction medium for the synthesis of many heterocyclic reactions over conventional solvents like ethanol, DMF,DMSO, THF and many more.. The major disadvantages of traditional solvents are their pyrophoric nature, volatility, and poor recovery. To address some of these issues, attempts have been made to develop solvent-free chemistry, which to some extent has been successful for a few transformations.[1] However, in performing the majority of organic transformations, solvents play a critical role in making the reaction homogeneous and allowing molecular interactions to be more efficient. In recent times ionic liquids have been in the forefront of research, and several publications and reviews have already appeared.[2] Even though ionic liquids offer some advantages, the tedious preparation of ionic liquids (and raw materials for ionic liquids) and their environmental safety is still debated. To address the concerns raised by volatile organic solvents, we initiated a new to identify whether any available liquid polymers or low melting polymers can be used as solvents.[3]

Recently, liquid polymers or low melting polymers have emerged as alternative green reaction media with unique properties such as thermal stability, commercial availability, non-volatility, immiscibility with a number of organic solvents and recyclability. PEGs are preferred over other polymers because they are inexpensive, completely non-halogenated, easily degradable and of low toxicity.[4] Many organic reactions have been carried out using PEGs as solvent or co-solvent such as Heck reaction,[5] asymmetric dihydroxylation,[6] Suzuki cross-coupling reaction,[7] oxydehydrogenation of alcohols and cyclic dienes, oxidation of sulfides and

the Wacker reaction[8] and partial reduction reaction of alkynes.[9] The use of PEG as a recyclable solvent system for the metal mediated radical polymerization of methyl methacrylate and styrene has also been reported.[10] Reducing or eliminating the use of organic solvents can minimize the generation of waste, which is a requirement of one of the principles of green chemistry. The demand for environmentally friendly reaction solvents to lower volatile organic compounds (VOCs) or toxic air emissions has grown, partly spurred by various government regulations. The use of water as solvent is probably the most desirable approach but this is often not possible due to the hydrophobic nature of the reactants and the sensitivity of many catalysts to aqueous conditions

Polyethylene glycol (PEG), known to be inexpensive, thermally stable, recoverable, biologically compatible, and non-toxic. PEG is most commonly employed as a support or a phase-transfer catalyst in various organic transformations. Its use as a reaction medium in organic reactions is relatively recent. In view of the current emphasis on green chemistry, our approach to reduces the use of solvents that are Volatile Organic Compounds (VOCs) which are potentially toxic and hazardous. Recently, PEG is found to be an interesting solvent system. The important difference between using PEG and other neoteric solvents is that all of the toxicological properties, the short and long-term hazards, and the biodegradability, etc., are established and known. PEG as environmentally benign protocol proved to have many applications particularly, in substitution, oxidation, and reduction reactions.

Following are the merits of PEG as solvent.

I. This reaction is convenient and efficient.
II. It has mild reaction condition.
III. It gives excellent yields of products.
IV. Starting material are easily prepared
V. Work up procedure and isolation is easier.
VI. Procedure is green and environmentally benign methodology.
VII. Shorter reaction time.

Following are the merits of PEG as solvent In Heterocyclic synthesis.

i. This reaction is more versatile, efficient and convenient.
ii. Short reaction time as compared to the reported method.
iii. It gives excellent yield and purity of the product.
iv. Work-up and isolation is easier.
v. PEG is a benign reaction medium than ethanol or other solvents.

vi. PEG is potentially recyclable reaction medium.

vii. PEG is nontoxic, being used in food products and cosmetics.

viii. Procedure is green and environmentally benign.

In continuation of our work on the synthesis of some new bioactive heterocyclic compounds PEG as greener reaction solvents over traditional solvents.[11-15]

An efficient and convenient procedure for the synthesis of thiazole derivatives from a-haloketone, thiourea and substituted acetophenones using polyethylene glycol-400 as a green and recyclable solvent is described. Significant rate enhancement and improved yields have been observed In view of the recent emphasis toward the development of new, selective, and environmental friendly methodologies using PEG-400 as a solvent for the synthesis of fine chemicals and biologically important compounds, herein we report an efficient method for the synthesis of thiazole derivatives by one-pot condensation of a-haloketone, thiourea, and substituted acetophenones using PEG-400 Initially we investigated the reaction of a-haloketone, thiourea, and 2-hydroxy-5-chloro acetophenone in PEG-400 at 408C to afford the corresponding product (4e) in 92% yield. In order to optimize the reaction conditions, we carried out the above reaction in different solvents, such as ethanol, dichloromethane, acetonitrile, isopropyl alcohol, benzene, and PEG-400 . We found PEG-400 an efficient reaction medium in terms of reaction time as well as yield (92%). This result encouraged us to carry out the reaction on several acetophenones in PEG-400 at 408C to afford the corresponding products in excellent yields Solvent effect on the reaction of a-haloketone, thiourea, and 2-hydroxy-5-chloro-acetophenone at 408C. Entry Solvent Time (min) Yield (%)1 EtOH 40 80 2 DCM 45 75 3 CH_3CN 35 82 4 IPA 40 84 5 C_6H_6 50 60 6 PEG-400 18 92 In summary, we have described a novel and efficient method for the synthesis of thiazole derivatives by one-pot condensation of a-haloketones, thiourea, and substituted acetophenones using PEG-400 as a green reaction medium. The present procedure has the advantage of reduced reaction times, mild reaction conditions, high yields, and greener aspects such as avoiding hazardous organic solvent, ease of recovery, and reuse of reaction medium, thus making it a worthwhile addition to the existing methods The above research has been elaborately discussed in my article titled *Eco-friendly polyethylene glycol-400: a rapid and efficient recyclable reaction medium for the synthesis of thiazole derivatives*

In continuation of our work on the synthesis of some new bioactive heterocyclic compounds PEG as greener reaction solvents over traditional solvents.

In another article we used PEG-400 as a solvent an efficient access, single step and environmentally benign synthesis of a new series of pyrazole containing isoxazolines derivatives were prepared by the condensation of chalcones bearing pyrazole moiety with hydroxyl amine

hydrochloride in basic condition by using polyethylene glycol-400 (PEG) as a greener reaction solvent. The advantages of the present methodology are mild reaction condition and avoidance of volatile organic solvent. Furthermore, these newly synthesized compounds were screened for their antimicrobial activity Emerging infection diseases and the increasing number of multi-drug resistant microbial pathogen still make the treatment of infection disease an important pressing global problem therefore a substantial research for the discovery and new class of antimicrobial agents is needed. Keeping in mind isoxazoline derivatives are useful as intermediates in the organic synthesis, are found to possess a wide important pharmacophore and privileged structure in medicinal chemistry In continuation of our work on the synthesis of some new bioactive heterocyclic compounds,21-23 herein we report new series of pyrazole containing isoxazolines derivatives was described here by the condensation of chalcones with hydroxyl amine hydrochloride in basic condition by using polyethylene glycol-400 (PEG) as a green reaction solvent. The starting chalcones are prepared by the reported method.24 Initially, we attempted the condensation of (5- chloro-2-hydroxy-3-iodophenyl)-3-(5-chloro-3-methyl-1- phenyl-1H-Pyrazol-4-yl)-prop-2-en-1-one (0.001 mmol) with hydroxyl amine hydrochloride (0.0015 mmol) in PEG- 400 (15 mL) as reaction solvent. The reaction went to completion and corresponding product (2a) was obtained in 90% yield.In summary, we have designed and synthesized some new pyrazole containing isoxazolines derivatives by the condensation of chalcones with hydroxyl amine hydrochloride in basic condition by using polyethylene glycol- 400 (PEG) as a green reaction solvent. The preliminary in vitro antimicrobial screening of this series revealed that, compounds showed potent activity. Therefore, the present study is useful for finding the new drugs in medicinal investigation against bacterial and fungal diseases. The above research has been elaborately discussed in my article titled *A Facile Greener Assisted Protocol for the Synthesis of Some New 4-aryl-(5-chloro-3-Methyl-1-pheny.-1H-Pyrazol-4-yl)-4,5-dihydroisoxazol-3-yl) Derivatives and there in vitro Antimicrobial activity*

In an another aticle related PEG 400 A new series of imidazole-containing 1, 5-benzodiazepines have been synthesized by the condensation of chalcones with ophenylenediamine using piperidine in polyethylene glycol (PEG-400) as an efficient and green reaction solvent. The advantages of this protocol are environmental friendliness, easy work-up, high yields, mild reaction condition and avoidance of expensive catalyst. Furthermore, newly synthesized compounds were evaluated for their antimicrobial activity. In summary, we have developed a novel, efficient and environmentally benign methodology towards the synthesis of 1,5-benzodiazepines by the condensation reaction of chalcones with o-phenylenediamine using

piperidine in polyethylene glycol (PEG-400) as an efficient and green reaction solvent is described. The advantages of the present protocol are the simplicity of operation, the high yields of products, the recyclability of PEG-400, avoidance of expensive catalyst and usage of volatile organic solvents. Antimicrobial data revealed that compounds carrying 2- hydroxy-3-iodo-5-chlorophenyl, 2-hydroxy-3-bromo-5-chlorophenyl, 2-hydroxy-3,5-diiodophenyl, 2-hydroxy-3,5-dibromophenyl and 2-hydroxy-3,5-dichlorophenyl were exhibited good antifungal and antibacterial activity. Therefore, the present study is more beneficial to the synthesis of new drugs with medicinal investigation against bacterial and fungal diseases The above research has been elaborately discussed in my article titled *Polyethylene glycol (PEG-400): An efficient and recyclable reaction medium for the synthesis of novel 1; 5-benzodiazepines and their antimicrobial activity*

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PEANUT SHELL AS AN ADSORBENT TO REMOVE MUREXIDE FROM AQUEOUS SOLUTION

A. Sahana, M. Poonkothai* and A. V. Swathilakshmi

Department of Zoology, School of Biosciences,

Avinashilingam Institute for Home Science and Higher Education for Women,

Coimbatore – 641043,Tamilnadu, India

*Corresponding author E–mail: poonkothaii_zoo@avinuty.ac.in

Abstract:

Release of synthetic dyes and industrial effluent systems and land have posed deleterious effect on the global community. An attempt has been made to highlight the potential of peanut shell in the adsorption of murexide from aqueous solution. The effect of process parameters such as dye concentration, adsorbent dose, pH, temperature and incubation time on the adsorption process was studied to establish the optimal experimental conditions with 0.1g of dye and 0.4g adsorbent at pH 5 and 30^{o}C on 4th day of incubation (84%) of colour was removed.The peanut shell was characterized by FT-IR spectral before and after murexide adsorption. FT-IR analysis revealed the presence of functional groups indicating the involvement of hydroxyl, alkyl, carboxyl and alkenes in adsorption of dyes. Phytotoxicity study was carried using *Vigna unguiculata L.*(Cow pea)for seven days and the biometric parameters were high in the dye degraded metabolites when compared with untreated dye solution. Hence peanut shell being a low-cost adsorbent can be explored in the large-scale level for the removal of colour from waste water.

Keywords: Murexide, Optimisation, FT-IR, Phytotoxicity.

Introduction:

With expanding population and modernized civilization there is a rise in the textile manufacturing industries in most part of the world.India is the second largest in exportingdye stuffs where 80,000 tons of dyes and pigments are produced annually (Saraswathi and Balakumar, 2009). One of the major problems that human beings are facing is the restoration of the contaminated environment. Textile dyes contribute the most important polluting agent of the ecosystem. Several classes of such contaminants have been synthesized and still new products

are being synthesized now and then. The textile industry consumes large amount of water and produces huge volumes of contaminated waste water thereby, rich in dissolved solids, ionic salt, pH, COD, color and heavy metal (Arulazhagan, 2016).

Textiles dyes generally are made of synthetic, organic and aromatic compounds that may contain some heavy metals in their structure. They are widely used in leather, paper, plastics, electroplating, cement, metal processing, textiles wood preservatives, paints, pigments and steel fabricating industries (Ponnusami *et al.,* 2008). These industries discharge large quantities of toxic wastes, and the untreated effluents from these industries cause soil and water pollution. Also, they behave as a mutagen, teratogen, and carcinogen. Induce dermatitis, affects the respiratory system function of human (Neta *et al.,* 2011).

Many efforts have been made to investigate the use of various techniques to remove dyes from waste water.A wide range of physical and chemical techniques are available for removal of toxic organic compounds from waste water but they often involve high investment and functional costs.Among all methods available for separation of pollutants from waste waters,the adsorption shows possible method for treatment and removal of organic pollutants in waste water treatment. Adsorption follows surface phenomenon and more advantageous over the other available methods because of its low capital, operation costs and simple design. In recent years agricultural and industrial wastes is used to remove hazardous contaminants from wastewater (Moghadam, 2010). However, as lower value agriculture waste peanut shells usage especially on an industrial scale, will yield economic as well as environmental dividends. With this background, an attempt has been made to study the "Peanut shell as an adsorbent to remove murexide from aqueous solution".

Methodology:

Collection and preparation of peanut shell

Figure 1: Peanut shell

Figure 2: Peanut shell powder

The peanut shell was collected from the local market of Karamadai, Coimbatore, Tamil Nadu and used as adsorbent for dye removal. The collected biomass was washed thoroughly with tap water to remove soil and dust, followed by distilled water and dried in an oven at 80°C for complete dryness (Fig 1). Dry peanut shell was crushed into powder and sieved through a mesh to get fine particles and stored in an air tight container for further use (Fig 2).

Batch adsorption study

The batch adsorbent experiments were conducted to optimize various parameters, namely dye concentration, pH, contact time, temperature and adsorbent dose for the color removal. The study was conducted in anErenmayerflaskby varying the concentration of dye (50-600mg) solution to which adsorbent (100-500mg) was added separately and incubated at different temperatures (20-60°C). The pH was varied from 2-10 using 0.1N NaOH and 0.1N HCl and the percentage decolourisation was recorded at incubation period (1-6 days) respectively.

At the end of predetermined time intervals, samples were withdrawn and the adsorbent was separated from the solution and the colour removal of the dye was recorded at 525nm. All experiments were carried out thrice with respect to each condition and the percentage decolourization was calculated using the formula

$$\text{Decolorisation (\%)} = \frac{\text{Initial absorbance of dye} - \text{final absorbance of dye}}{\text{Initial adsorbance of dye}} \text{ x100}$$

Under the optimal conditions, the known concentration of peanut shell was added into murexide dye solution and the percentage decolourisation was determined.

Desorption of dye

The dye adsorbed peanut shell was harvested, washed twice with distilled water and dried.The dried peanut shell (0.4g) was taken in 250ml Erlenmeyer flasks containing 100ml of each eluting reagent namely 0.1 NaOH and 0.1N HCl separately. The flasks were agitated for 30 minutes in shaker at 110 rpm. The liquid samples were withdrawn, centrifuged and analyzed for optical density to determine color intensity in the liquid using UV-VIS spectrophotometer. The desorbed biomass separated from the liquid phase was also mechanically destructed, grinded and washed with distilled water to remove colour from the peanut shell and analyzed for optical density.

FT-IR Spectroscopy

To determine the functional groups that are responsible for decolourisation in dye-loaded and unloaded peanut shell was observed using FT-IR Spectrophotometer (Shimadzu, Japan). The

samples were then mixed with KBr pellets, in the mid IR range of 400- 4000 Cm-1 at 16 scan speed.

Phytotoxicity study

In this experiment the effect of murexide dye at the concentration of 1g/L was evaluated on seed germination and seedling growth of *Vigna unguiculata.*L. The seeds were germinated in pots containing equal proportion of red soil and sand. Experimental set up included nine pots arranged in three sets for three different treatments with three replicates for each treatment. Five seeds were sown in each pot and were watered every 24 hours using tap water (T_1) untreated dye solution (T_2), and treated dye solution (T_3). Seed germinated in pots using tap water was used as control. All pots were kept under shade near sunlight for a period of seven days. Germination percentage of seeds in all treatment was recorded. At the end of the experiment the plants were uprooted carefully without damaging the roots. The shoot length, root length and fresh weight of seeding were measured separately for each treatment.

Results and Discussion:

Optimization studies for murexide decolourisation using peanut shell

Initial concentration provides a significant driving force to overcome all the mass transfer resistance of the dye between the solid and aqueous phases and thereby increases the uptake. Hence dye concentration plays an important role in the removal of colour from the aqueous solution (Lv *et al.,* 2013). The murexide at the concentration of 100mg showed maximum decolourisation (77%) by peanut shell at 4 days of incubation and minimum decolourisation (31%) was observed at 600mg. From the Fig 3a, it was clear that by increasing the dye concentration the rate of decolourisation decreases considerably.The effect of initial dye concentration depends on the immediate relation between the dye concentration and the available bindings sites on an adsorbent surface (Umorenet *et al.,* 2013). At high concentration the available sites of adsorption become fewer and hence the percentage removal of dyes gets decreased with increase in initial dye concentration (Mohandass and Ganesan, 2016). Jin (2015) carried out the bioadsorption study at different dye concentrations ranging from 40mg/L to 240mg/L. The percentage adsorption of crystal violet from aqueous solution onto almond shell decreases with increasing initial dye concentration. The decrease in percentage adsorption with increasing dye concentration is due to the saturation of available active sites of the adsorbents at higher concentration of dye molecules.

Adsorbent dose is important parameters influencing the adsorption processes since it determine the adsorbent capacity of an adsorbent for a given initial concentration of the

adsorbent at the operating conditions (Kushwaha *et al.,* 2014). The percentage removal of murexide was studied by varying the adsorbent dose between 100mg and 500mg at a dye concentration of 100 mg/100ml. The removal increased with increased amount of peanut shell up to 400mg with a maximum efficiency of 78% thereafter an increase in adsorbent dosage does not further improve the dye removal, implying that a complete dye removal could not be achieved even though using large amount of the adsorbents (Fig 3b). When too much adsorbent was added into the dye solution, the transportation of dye ions to the active adsorption sites will be limited and thereby the adsorption efficiency was reduced (Gode and Pehlivan, 2005). Cao *et al.* (2014) explained that the adsorption capacity of almond shell decreased with increasing adsorbent dose which may be due to the aggregation of the adsorbent particles on the active surface of the adsorbent. The adsorbent remains unavailable for the binding of dye molecules and it results in the decrease of adsorbent capacity.

Contact time can be effective on adsorption processes. The effect of contact time was observed for a varying time period from 1 to 6 days and the results revealed that the percentage decolourisation of murexide by peanut shell was (84%) at 4th day of incubation (Fig 3c). Therefore, equilibrium time of 4 days was selected for the adsorption of the dye for further studies.The rate of removal of the adsorbate is higher in the beginning due to the large surface area of the adsorbent available for the adsorption of dye ions (Hameed and Ahmad, 2009). After a certain period, onlyuptake of dye was observed because there are few active sites on the surface of sorbent and saturation of the sorption sites on the adsorbents as the concentration of the dye increased might occur. A similar observation was reported for the adsorption of malachite green on oil palm trunk fibre (Hameed and Khaiary, 2008).

pH is a key parameter that enhance dye adsorption and its rate varies with the pH of an aqueous medium. The pH of a medium controls the magnitude of electrostatic charge which is important for the ionised dye molecules (Onal *et al.,* 2006) and Ansari *et al.,* 2011). Solution pH is one of the most critical parameters in the adsorption process and pollutants removal from aqueous solutions (Mahvi *et al.,* 2012) and Shokoohi (2010).The effect of pH on murexide adsorption was studied in the range of 2 to 10. The adsorption capacity for the peanut shell was maximum at pH 5 (84%) and further increases in pH gradually decrease the adsorption percentage and minimum of 18% adsorption was recorded at pH 10 (Fig 3d). The electrostatic attraction as well as the organic properties of the adsorbent and structure of dye molecules plays an important role in dye adsorption. Thus, a competition between the protons and hydroxyl ions for adsorption occurs. Under acidic condition the dye uptake is higher as compared to the basic

and neutral conditions. When pH is raised the charge of the dye becomes negative and the interaction between the dye and adsorbent decrease which in decrease in adsorption of dye. The surface of the adsorption peanutshell has hydroxyl ions (OH^-). This might have completed with the dye which is acidic in nature when dissolved in water.Thus, the pH value of the solution is an important process controlling parameter in the adsorption of dye. At an acidic pH condition, the hydroxyl groups on the surface of peanut shell get attracted to the dye and promote the binding of dye.

Temperature is significant parameters because it will change the adsorption capacity of adsorbent (Argun *et al.,* 2009). It has two significant effects on the adsorption. Increasing the temperature has a known effect to increase the rate of diffusion of the adsorbate molecules across the external boundary layer and in the internal pores of the adsorbent particle, owing to the decrease in the viscosity of the solution. In addition, changing the temperature will change the equilibrium capacity of the adsorbent for a particular adsorbate (Alkan *et al.,* 2008) and Tekin *et al.,* 2005). The effect of temperature was studied in the range of 20°C to 60° C. The percentage dye removal was maximum at 30ºC (72%) and further increases in temperature from 40° C to 60° C could not increase the dye removal capacity instead a decrease was observed from 46 % to 11% respectively. The observations showed the optimum temperature for dye removal was noticed to be 30°C (Fig 3e).The initial increase in the adsorption rate may be due to increase in surface area of the adsorbent. Further increase in temperature could result in the loss of active surface area due to prolonged exposure to high temperatures which have resulted in low dye removal at higher temperature. Rehman *et al.* (2013) also explained that at higher and lower temperature, adsorption efficiency of dye decreases. This decrease in adsorption efficiency was attributed to the fact that at high temperature murexide and brilliant vital red dyes molecules move with larger speed and less time of interaction was available for the adsorbate with urea modified rice husk.

From the batch adsorption studies it wasconcluded that the most efficient operational parameters in the current study were found to be, pH of 5, temperature of 30°C, adsorbent dose of 0.4g, and contact time of 4^{th} day (peanut shell) for the decolourisation of 0.1gm of murexide dye solution using peanut shell (Fig 4a&b).

Desorption of murexide dye

The extent of desorption of colour from the adsorbent depends upon the hydration of dyes, functional groups of the cell wall and their respective binding strength. Desorption experiments were conducted with peanut shell using 0.1N HCl and 0.1N NaOH so as not to

destruct adsorbent structure. A marginal desorption (10%) of the sorbedcolour was observed with distilled water. Maximum desorption of 70% for 30 minutes contact time using 0.1N HCl was observed in peanut shell whereas 0.1N NaOH desorbed only 52% of dye from the aqueous solution. No significant increase in desorption of color was observed with increased contact time between the bio adsorbent and the eluting agent.

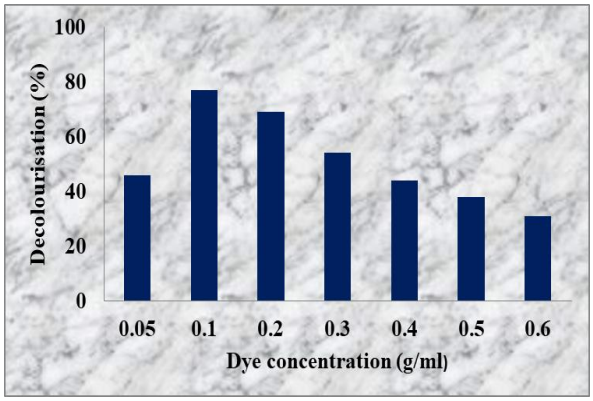


Figure 3a: Effect of dye concentration on murexide decolourisation by peanut shell

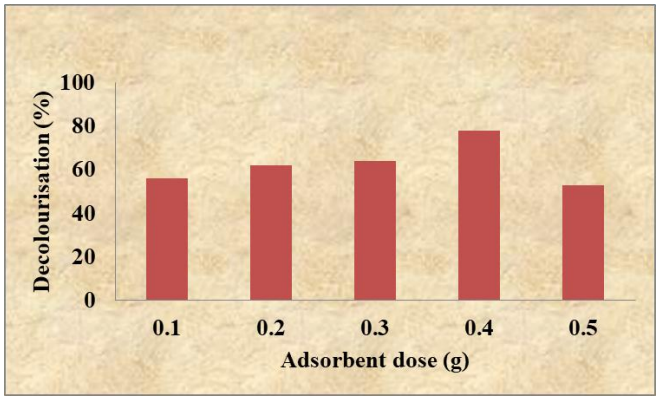


Figure 3b: Effect of adsorbent dose on murexide decolourisation by peanut shell

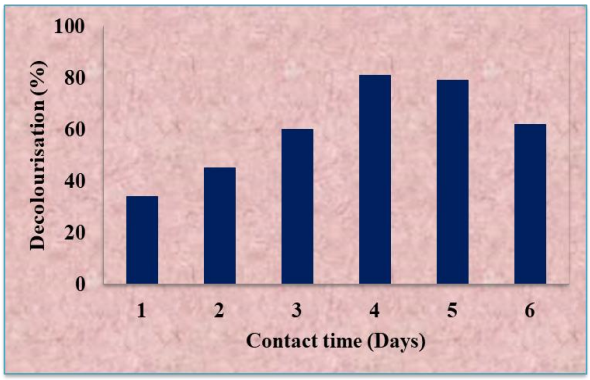


Figure 3c: Effect of contact time on murexide decolourisation by peanut shell

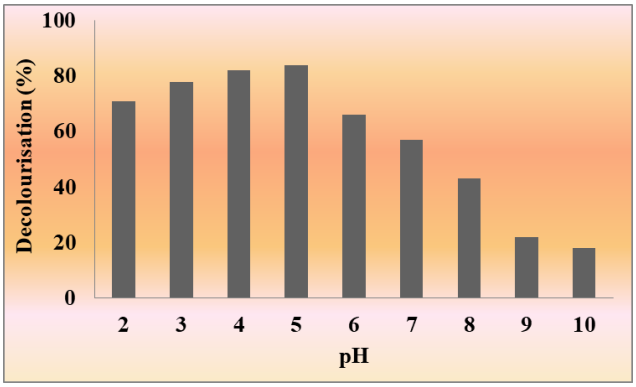


Figure 3d: Effect of pH on murexide decolourisation by peanut shell

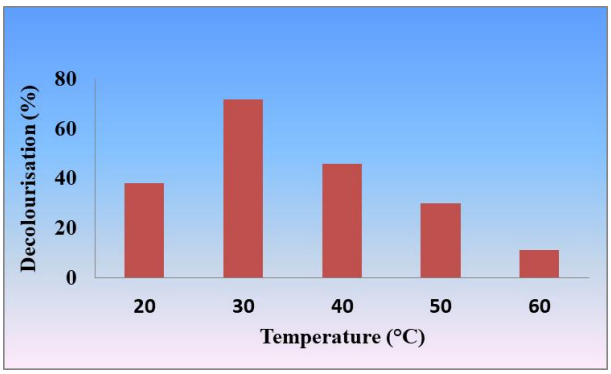
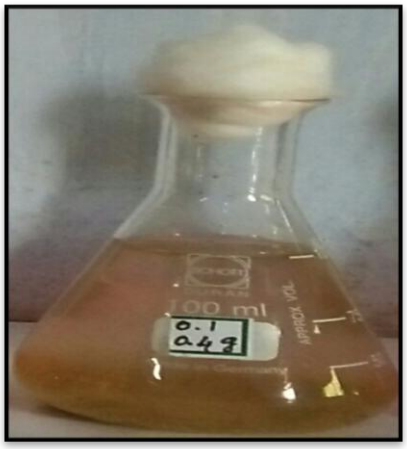


Figure 3e: Effect of temperature on murexide decolourisation by peanut shell



A. Untreated murexide dye **B. Treated murexide using peanut shell**

Figure 4a&b: Decolourisation of murexide using peanut shell species under optimal conditions

FT-IR Spectra of dye loaded and unloaded peanut shell

The dry powdered samples of peanut shell were subjected to Fourier Transform Infra-Red analysis which resulted in many functional groups based on the wavelength and percentage of transmittance. The complex nature of the biomass examined is indicated by a number of absorption peaks in the control sample. The spectra of decolourised sampled reveals shift in the characteristic bands, which depict changes in functional group after decolourisation compared to untreated dye sample.

The band at 3410.15 cm^{-1} was shifted to 3433.29 cm^{-1} due to O-H stretching vibration, which indicates the presence of alcohols and phenols. The peak shift from 1257.59 cm^{-1} to 1265.30 cm^{-1} is due to C-O stretching and 1153.43 cm^{-1} to 1157.29 cm^{-1} represents the C=O stretching vibrations and the presence of amide groups. Minor peaks at a 509.21 cm^{-1} to 478.35 cm^{-1} indicate the involvement of S-O groups in the decolourisation of the dye. New peaks (2337.72, 2291.43, 2167.99, 2086.98, 2067.69, 2032.97, 1994.40, 1978.97, 1724.36, 1724.36, 1265.30 cm^{-1}) were noted in the dye treated solution with peanut shell indicating the decolourisation of the dye.On the basis of the change in the band, it was reasonable to assume that the peak value suggested the coordination of the dye with hydroxyl or carboxyl or amino groups, which may increase the hydrogen bodings or forms ligands between the dye and the cell wall.Considerable difference between the FT-IR spectrum of control

murexide and the metabolites obtained after complete decolourization by peanut shell confirmed the biodegradation of dye into different metabolites (Fig 5a &5b).

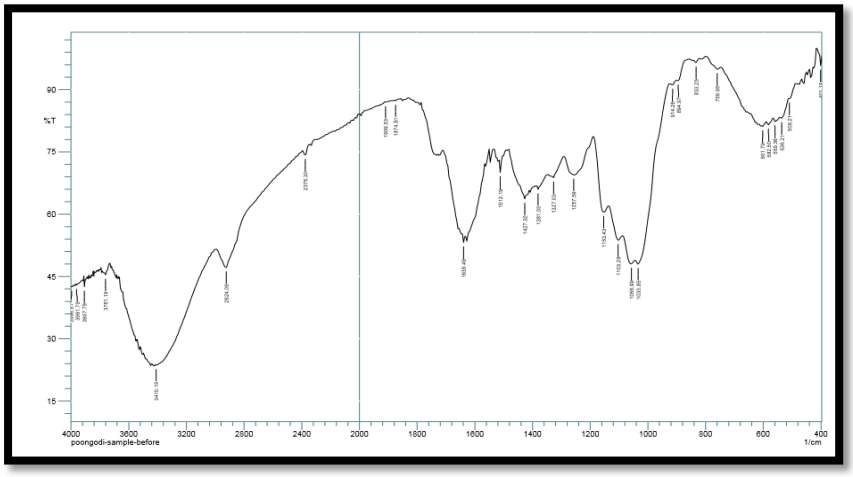


Figure 5a: FT-IR spectrum of peanut shell before adsorption

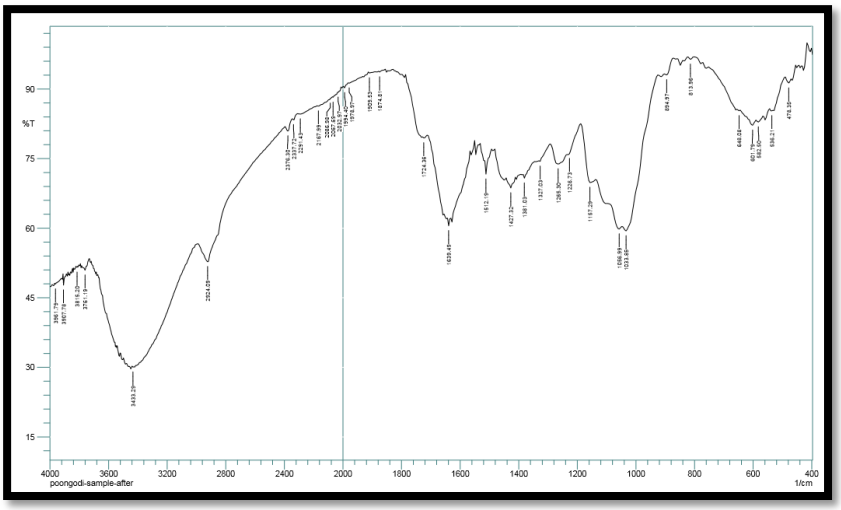


Figure 5b: FT-IR spectrum of peanut shell after adsorption

Phytotoxicity study

The result revealed that the germination percentage, root length, shoot length, fresh weight, dry weight and vigour index in *Vigna unguiculata L* seedlings exhibited the maximum growth in tap water (T_1) followed by treated murexide (T_3) and minimum was observed in untreated murexide (T_2) .Fig 6 shows the growth of cow pea on 7th day. A maximum of 85% germination was recorded in cow pea seeds grown with tap water (T_1) followed by 52 percent in treated dye solution (T_3). A minimum of 6 percent germination was recorded in seeds grown with untreated dye solution (T_1). The vigour index was maximum in T_1 (1752) followed by T_3 (764) and minimum was observed in T_2 (25) as shown in table 1. Decrease in the vigour of seeds

irrigated with untreated murexide observed in the present study might be due to the interaction of different pollutants with the developing radical.

Shoot length of seven days old cow pea seedlings after treatment with tap water (T_1), untreated murexide dye (T_2), and treated dye (T_3) were recorded in Fig 7 shows the shoot length and root length of 7 days old cow pea.The values recorded for the shoot lengths of cow pea seedlings were 12.2, 1.0 and 9.83 cm in T_1, T_2 and T_3 respectively. The values recorded for the seedlings grown in treated dye (T_3) were highly significant when compared with untreated dye (T_2). The root length of *Vigna unguiculata L* was maximum (7.6cm) in T_1, followed by T_3 (3cm) and minimum (0.22 cm) in T_2. T_1 showed an increase in root length when compared to T_2 and T_3 plants. From the above results it was observed that the reduction in shoot and root length of seedlings grown using T_1 might be due to the presence of higher dye concentration of dye which exhibited the uptake of micro and macro elements by plant system. Murexide treated with peanut shell has been reported to favour root and shoot length due to the translocation of nutrients to the plants (Jothimani and Elayarajan, 2003).

The fresh weight of cow pea seedlings treated with different treatments was depicted in Table 1. The highest fresh weight (0.42 g) was observed in T_1, followed by treated dye T_3 (0.20 g) and least value (0.20 g) was recorded in T_2. The dry weight of cow pea was maximum (0.21 g) in T_1 and minimum (0.030 g) in T_2 and T_3 recorded (0.136 cm). There was an increase in the fresh and dry weight of T_1 plants when compared with treated dye and T_2 plants. The reduction in the fresh and dry weight of the cow pea plants selected for the present study may be due to the physiological stress caused by the dye which restricted the plant growth by increasing the soil osmotic pressure (Jothimani and Elayarajan, 2003).

Figure 6: Pot culture supporting the growth of 7 days old *Vigna unguiculata L*

Figure 7: Root length and shoot length of 7 days old *Vigna unguiculata L*

Table 1: Biometric parameters in 7 days old seedlings of *Vigna unguiculata L*grown with different treatments

Treatments	Germination percentage	Shoot length (cm)	Root length (cm)	Fresh weight (g)	Dry weight (g)	Vigour index
T_1	85	12.2	7.60	0.42	0.210	1752
T_2	6	1.0	0.22	0.05	0.030	25
T_3	52	9.83	3.0	0.20	0.135	764
SED		0.7524	0.7824	0.0308	0.0175	
CD (5 %)		2.1545	2.0121	0.1126	0.0412	

The values are mean of triplicates

T_1 – Tap water, T_2 – Untreated murexide dye solution, T_3 – Treated murexide dye solution

Conclusion:

The present study concluded that the low - cost adsorbent like peanut shell has the potential for the decolourization of murexide dye. The phytotoxicity study also revealed that the treated dye solution is non-toxic and can be utilized for agricultural purpose.

Acknowledgement:

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EXPLORING THE UNEXPLORED NATURAL PRODUCTS: FUTURE PERSPECTIVES FOR THE BIOPROSPECTING OF CNIDARIANS

Pramitha, V. S[1]. and Sreejith Parameswara Panicker[2]*

[1]Department of Aquatic Biology and Fisheries, University of Kerala,

Thiruvananthapuram 695 581

[2]*Department of Zoology,

University of Kerala, Thiruvananthapuram 695 581

*Corresponding author E-mail: p.sreejith@gmail.com, psreejith@keralauniversity.ac.in

Abstract:

Marine invertebrates are the richest and prominent source of marine natural products with potential applications in the pharmaceutical and industrial sectors. With growing bioprospecting efforts and the screening of previously unexplored marine habitats, nearly 20 000 compounds have been discovered so far. In this context, the marine cnidarians assume greater significance as they rank second (18%) in contributing natural products with pharmacological properties. It has been reported that over 3,000 bioactive compounds have been described from this phylum alone. Among the different groups of marine cnidarians, the anthozoans in general and the soft corals and sea fans have contributed with the highest percentage (78%) of promising bioactive marine compounds, followed by the sea anemones and hard corals. On the other hand, only a few of the hydrozoans have yielded promising marine natural products. Among the different species of scyphozoans only the species *Aurelia aurita* has yielded a single antibacterial marine natural product. It has also been estimated that the bioactive compounds of marine cnidarians have showedantitumour (41%), antimicrobial (24%) and anti-inflammatory (22%) activities. From an analysis aspect, this chapter aims to emphasize and update the current knowledge reported on selected biological activity and highlighting potential aspects for ongoing research towards their utilization in human therapeutic approaches. The present chapter also discusses future perspectives and roles for the bioprospecting of new MNPs produced by this species group of marine invertebrates.

Keywords: Cnidarians, Drug discovery, Natural Compounds,Venoms

Introduction:

The phylum Cnidaria is a large and ecologically important group of marine invertebrates including corals, sea fans, sea anemones and jellyfishes. These cnidarians with about 11,000 extant species were previously grouped with ctenophores in the phylum Coelenterata, but increasing awareness of their importance and differences from acnidarians prompted Cnidaria to be placed as a separate phylum (Jain *et al*. 2008) and 99% cnidarians are reported as marine species. The phylum Cnidaria includes the major classes likeHydrozoa (fire corals, hydroids, hydroid jellyfishes, siphonophores), Scyphozoa ('true' jellyfishes), Cubozoa (box jellies) and Anthozoa (tube-dwelling anemones, stony corals, soft corals and sea fans) (Hill and Fenical, 2010).

Potential of marine cnidarians as a drug source

Marine cnidarians are considered as treasures that remain a relatively unexplored source for novel bioactive compounds. More than 3000 compounds have been described and the isolated compounds like alkaloids, sterols, sesquiterpenes, diterpenes, terpenoids, steroids andeicosanoids have been found not only to be active against infectious diseases such as human immunodeficiency virus (HIV), malaria and tuberculosis but also have other relevant biological activities, including anti-inflammatory, antifouling and antitumor activities (Brinkman and Burnell, 2009). However, out of the total 11, 000 species, only 302 species (2.8%) have been reported to yield natural products. Out of 7041 species of class Anthozoa, 300 species (4.3%) have yielded natural products. Further, the order Alcyonacea assumed greater importance and out of the 3243 species, 257 species (7.9%) have yielded natural compounds. These findings and reports suggest that intensive research is further needed on marine cnidarians for the exploration of natural products of therapeutic importance. However, it was also observed that, none of the identified compounds extracted from marine cnidarians have been effectively developed as drugs. Nevertheless, pseudopterosin extracted from the sea whip and *Erythropodium caribaeorum* and sarcodictyns has been employed in preclinical studies. The compounds isolated from the marine Cnidarian species have been found to possess antitumour (41%), antimicrobial (24%) and anti-inflammatory (22%) activities (Blunt *et al*. 2015; Blunt *et al*. 2016).

Venomous marine cnidarians

It was estimated that about 100 species of cnidarians are potentially dangerous to humans, and the Cubozoans are believed to be the deadliest. The Australian stinger *Chironex fleckeri* caused human fatalities, is considered as the deadliest creatures in the world and this species has been previously reported to be responsible for more than 70 fatal stings and known to

cause 'Irukandji syndrome, a condition characterized by excruciating muscle pain, vomiting, increased heart rate and psychological symptoms. It was also studied that the hydrozoan jellyfish *Olindiassam baquiensis* has also contributed to mild incidents in the form of lesions on the southeastern and southern Brazilian coast, where it is commonly found in winter and autumn (Haddad *et al*. 2014).

Role of cnidarians in molecular studies

Compounds and toxins from Cnidaria have attracted attention, not only for their effects on humans, but also could act as very useful molecular probes for the study and analysis of ion channels involved in electrical signaling and immune responses, which might have biomedical interest (Frazao *et al*. 2017). Crude venom extracted from cnidarians haveelicited wide range of effects on humans, such as dermonecrosis, edema, diffused neurotoxicity, motorial and respiratory problems, cardiovascular symptoms, hypotension and occasionally death.The common effects observed are cytotoxic, cytolytic, hemolytic and neurotoxic. It was also analysed that Cnidaria venoms might contain enzymes, pore-forming toxins, neurotoxins and enzyme inhibitors. Cnidariapeptide named ShK-186 or dalazatide, is currently in clinical trials for the treatment of autoimmune diseases. In particular, dalazatide is a potassium channel (Kv1.3) blocker and has successfully completed Phase 1 within clinical trials and is about to enter Phase 2 of the trials for the treatment of multiple sclerosis and rheumatoid arthritis. Global neuropeptide annotations isolated from the genomes and transcriptomes of Subozoa, Scyphozoa, Staurozoa (Cnidaria: Medusozoa), and Octocorallia (Cnidaria: Anthozoa) (Turk and Kem, 2009).

Venom components have been shown to possess interesting bioactivities for possible pharmaceutical applications. Several compounds from Cnidariahas showed cytotoxic and cytolytic activities on various mouse and human cell lines (Jaimes-Becerra *et al*. 2017). Studies also tested cnidarian compounds on normal cells in order to show their selectivity. Compounds/extracts from Cnidaria exhibited activity against leukemia, colon carcinoma, lymphoma, lung adenocarcinoma, glioblastoma, melanoma, ovarian adenocarcinoma, breast adenocarcinoma, cervix carcinoma, epidermoid carcinoma, glioblastoma, hepatoma, pheochromocytoma, prostate and pancreatic carcinoma, fibrosarcoma, renal and central nervous system cancer. Five new polyoxygenated marine steroids, named punicinols A, B, C, D and E, were also isolated from the gorgonian *Leptogorgia punicea* (Anthozoa, Octocorallia) and showed *in vitro* cytotoxic activity against human lung cancer A549 cells. Punicinols A and B were also tested in combination with paclitaxel, a well-known cytotoxic compound, and showed synergistic effects. Cell-cycle analysis also showed that punicinol A induced the arrest of the Sub G0/G1, while punicinol B the G2M phase. Punicinols A and B also showed effects on the

clonogenic potential of A549 cells, completely inhibiting the growth of cancer cells after 24 h of treatment and 10 days for cell proliferation monitoring. Further studies could clarify punicinols A and B activity and may propose them combined with paclitaxel in tumor chemotherapy (Ponce *et al*. 2016).

Additionally, *Pelagia noctiluca* (Scyphozoa) venom constituents has showed anticancer and anti-inflammatory activities and its venom was fractioned using Sephadex G75.Four fractions were obtained and their anti-proliferative activity was also tested on three cancer cell lines like human bladder carcinoma RT112, glioblastoma U87 and human myelogenousleukemia K562 and on human peripheral blood mononuclear cells (PBMC) obtained from the blood of healthy volunteers (Rachamim *et al*. 2015).

Considering the increasing human consumption of sea anemones as food, studies also evaluated the effects of aqueous extracts, in order to mimic the route of ingestion. Two species of sea anemones, *Actinia equina* and *Anemonia sulcata* exhibited major compounds like methylpyridinium alkaloid and homarine and tested their cytotoxic effects against murine RAW 264.7 macrophages. *In vitro* anti-inflammatory activity of the two extracts and homarine was also evaluated in a murine macrophage model of inflammation, using a lipopolysaccharide (LPS)-induced RAW264.7 cell line. Results showed that they were able to reduce the LPS-induced levels of NO and intracellular reactive oxygen species (ROS) in macrophages and that both extracts and homarine were able to inhibit phospholipase A_2, a pivotal enzyme in the initial steps of the inflammatory process. Finally, possible cytotoxicity on human gastric adenocarcinoma cells (AGS) was also tested. After 24 h, the cytotoxic effect of both extracts was concentration-dependent in the same concentration range. Homarine was found tobecytotoxic as well, causing decreased cell viability by 27.57% ± 5.42% at the highest concentration. On the contrary, caspase-4 activity was increased after incubation with the aqueous extracts of *A. sulcata* and homarine. Altogether, these data suggests a non-classical mechanism of apoptosis mediated by caspase-4 and -3 in human gastric cells. The study gave new insights on the toxicity and biological potential of the two sea anemones, which are increasingly used in human nutrition (Lohr *et al*. 2019).

Anti-inflammatory activity was also noted for other sea anemones and considered as the richest sources of Kunitz-type polypeptides, which can have proteinase inhibitory, Kv channels toxicity, analgesic, antihistamine and anti-inflammatory activities. Two Kunitz-type inhibitors from the sea anemone *H. crispa*, named HCRG1 and HCRG2 showed anti-inflammatory activity by reducing the secretion of the pro-inflammatory mediators (Edwards *et al*. 2002).

The HCGS recombinant polypeptide from the same sea anemone species showed anti-inflammatory activity by inhibiting the histamine-induced increase in the concentration of calcium ions in mouse bone marrow-derived macrophages and the lipopolysaccharide-stimulated increase in the concentration of nitric oxide in RAW 264.7 mouse macrophages. Successively, two recombinant peptides, the Kunitz-type serine protease inhibitors rHCGS1.19 and rHCGS1.36, from *H. crispa* showed antihistamine activity at 10 μM, inhibiting an increase in the calcium ion concentration in murine bone marrow-derived macrophages elicited by histamine at 62.2 and 84.0%, respectively. HCGS1.36 and HCGS1.10 have also showed analgesic effects in the thermal pain stimulation model at a concentration of 0.5 mg/kg (Marino *et al*. 2007).

Sea anemones have also excellent sources of human pancreatic α-amylase inhibitors with possible applications in the control of blood sugar levels in the management of diabetes mellitus patients. In particular, helianthamide was isolated from the Caribbean Sea anemone *Stichodactyla helianthus* and showed to adopt a β-defensin fold and bind into and across the amylase active site.Magnificamide, recently isolated from sea anemone *Heteractis magnifica*, shared 84% sequence identity with helianthamide and inhibited porcine pancreatic and human saliva α-amylases with Ki's equal to 0.17 ± 0.06 nM and 7.7 ± 1.5 nM, respectively, showing to be another potential drug candidate for diabetes treatment (Brinkman *et al*. 2012).

Venom proteins identified in the Cubomedusa *Chironex fleckeri*, CfTX-1, CfTX-2, CfTX-A and CfTX-B, showed possible cardiovascular and cytolytic applications. Recently, a new metalloproteinase was identified and partially purified from *Rhizostoma pulmo* (Scyphozoa) and this metalloproteinase showed significant hemolytic activity against human red blood cells and a strong proteolytic activity for substrates like (azo) casein and gelatin. With the urgent need to discover and develop new antibiotics, several studies have explored the antimicrobial/antibiotic properties of cnidarian extracts. However, due to sampling difficulties and extracting low amounts, very few proceeded in pre-clinical evaluation (Mariottini *et al*. 2002).

Role of cnidarian venoms in drug discovery

The toxic compounds isolated from Cnidariahas been viewed to induce several implications to human health like neurotoxicity, cytotoxicity and tissue damage. Recent findings have demonstrated that their toxins could offer a tool to study cell physiology and provide promising sources of pharmacological lead/active agents for the therapy of human diseases.Palytoxin, a highly potent non-protein toxin isolated from the soft corals *Palythoa* spp. and *Zoanthus* spp., and the sea anemone *Radianthus macrodactylus* have been reported for their anticancer activity against head and neck carcinoma cells, Ehrlich ascites tumour and P-388 lymphocytic leukaemia cells. Further, several cytolysins and protease inhibitors have been

extracted from the sea anemone *Actinia equina*. Equinatoxin II has been showed to have a significant toxicity against Ehrlich ascites tumour and L1210 leukaemia cell lines and diploid lung fibroblasts of the Chinese hamster (Mariottini and Pane, 2013).

Antibutyrylcholinestrasic activity has been detected in the crude venom extracted from the tentacle material of the Mediterranean jellyfish *Pelagia noctiluca*. The inhibition of butylcholinestrase in the central nervous system may prove useful in the treatment of neurodegenerative diseases such as Alzheimer's disease and senile dementia (Nagai *et al*. 2002). Stichodactyla toxin (ShK), a potent channel blocker toxin isolated from the sea anemone *Stoichactis helianthus* could provide a valuable immunosuppressant for the treatment of autoimmune diseases mediated by T cells (lymphocytes). Kv1.3 blockers are also considered as therapeutic target for the treatment of obesity, thus highlighting the potential use of treatment of obesity and insulin resistance (Marrero *et al*. 2006).

Nemopilema nomurai jelly fish venom (NnV) has been reported to possess anticancer activity andNnV strongly induce the cytotoxicity of HepG2 cells through apoptotic cell death. Of the total cnidarian species, only 156 toxins from 10 pharmacological families hasbeen reported so far. The enormous potential of cnidarian venoms as sources of novel pharmaceutical lead compounds appears to offer endless possibilities for future scientific research (Marrero*et al*. 2003).

Constraints associated with natural products of marine cnidarians

Sustainable supply of bioactive compounds from pharmaceutically important species of marine cnidarians may pose problems, owing to their presence in low quantities or difficulties in their isolation. This could be overcome by undertaking the 'mariculture' of such cnidarian species. Further, the lack of taxonomic knowledge of marine cnidarians species may also be a major blockage, as improper taxonomic knowledge and identification of a natural product-yielding species may make the entire exercise futile (Shiomi *et al*. 1989).Table 1 indicates list of most promising compounds isolated from Cnidarian species.Fig. 1-3 accounts marine bioactive compounds with high biotechnological potential from phylum Cnidaria.

Table 1: List of most promising compounds from Cnidarian species

Species	Drug class	Compound	Chemistry
Klyxum simplex	Anti-inflammatory	Simplexin E	Diterpenoid
Klyxum simplex	Antitumor	Klysimplexin B and H	Diterpenoid
Lobophytum sp.	Antitumor	Lobophytene	Diterpenoid
Sarcophytoncrassocaule	Antitumor	Crassocolides H–M	Cembranoid
Sinulariaflexibilis	Antifoulant	episinulariolide	Diterpenoid
Sinulariagibberosa	Anti-inflammatory	Gibberoketosterol	Steroid
Sinulariaquerciformis	Anti-inflammatory	Querciformolide C	Terpenoid
Clavulariakoellikeri	Antitumor	Cembrane-type diterpenoid	Diterpenoid
Clavulariaviridis	Antitumor	Claviridenone	Prostanoid
Dendronephthyarubeola	Antitumour	Capnell-9(12)-ene-8β,10α-diol	Sesquiterpenoid
Xenia plicata	Antitumor	Blumiolide C	Diterpenoid
Dendronephthya sp.	Antifoulant	Isogosterones A–D	Steroid
Nephtheachabroli	Antitumor	Chabranol	Terpenoid
Nephtheaerecta	Anti-inflammatory	Ergostanoids 1 and 3	Ergostanoid

Fig.2. Distribution of drug classes with high potential from Cnidaria

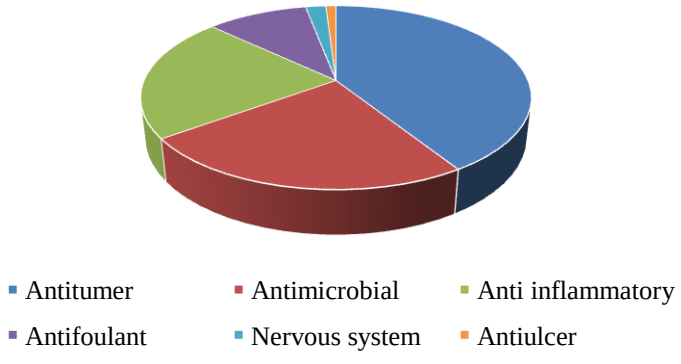
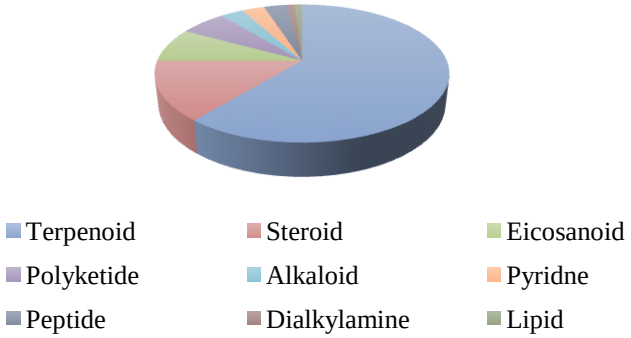


Fig.3. List of chemistry classes of compounds with high potential from Cnidaria



Conclusions:

The intense pressure to find and develop more profitable molecules paved the way to fuel the bioprospecting of marine invertebrates. Natural compounds from marine organisms has been considered slightly in pharmacology and have had limited therapeutical application. Cnidarians are gelatinous invertebrates, in large part inhabiting seawaters, which play an important role among venom-producing organisms and are viewed with particular concern owing to the implications of their stings on human health and on economy. Cnidarian species are promising sources of marine bioactive compounds of medical, economic and scientific interest. Antitumor drugs are the main area of interest in the screening of MNPs from cnidarians (41%). New compounds other than toxins and venoms produced by members of this highly diverse group of marine invertebrates may be discovered in the quest for new marine products. Cnidarian tentacles and/or oral arms, and at times the whole body, are armed with nematocysts, specialized venom-containing structures provided with a tightly wrapped and spiralized thread used to inject the venom. Cnidariapossess cytotoxic, hemolytic, anti-inflammatory, antitumoral, anti-infective, anti-parasite, as well as other interesting properties and this chapter reviewed about cnidarian properties that could be of concern for drug discovery as potential sources for pharmaceuticals.

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About Editors

Dr. Suraj B. Ade is working as Associate Professor in the Department of Chemistry and Analytical Chemistry, MSP Mandal's Shri Shivaji College, Parbhani. He got his M.Sc., Degree in Organic Chemistry from Sant Gadge Baba Amravati University, Amaravati in 1998 and Qualified NET examination in 2001.He has awarded Ph.D. Degree in 2013 by Swami Ramanand Teerth Marathwada University, Nanded. He is a Recognized Research Supervisor and Post Graduate Teacher. He has been teaching for under graduate students for last 19 years and 09 years of research experience. He has also participated in many National, International, and State-level seminars, Conferences, and Workshops where he read his scholarly papers. He has published 39 research papers in National and International Journals and two edited books to his credit and also two books published in Analytical Chemistry for B. Sc. I year (Semester I and II).

Dr. Omprakash S. Chavan has completed M.Sc. Organic Chemistry from Depatrtment of Chemistry, Dr. B. A. M. University, Aurangabad, Maharashtra. He qualified SLET in August 2004, CSIR-NET-LS in June 2005 and CSIR-NET-JRF in December 2005. He awarded with Ph.D. degree from S. R. T. M. University, Nanded, Maharashtra. He published more than 25 research papers in reputed, referred, National and International Journal. Now, Dr. Chavan is working as an Associate Professor at Department of Chemistry, Badrinarayan Barwale College, Jalna, Maharashtra, India, since 2005.

Dr. Arshia Parveen working as an Assistant Professor, Department of Chemistry, B. Raghunath ACS College, Parbhani completed her Ph.D from SRTMU, Nanded in 2011 and M.Phil from Madurai Kamaraj University, Tamil Nadu in 2007. Her area of interest is Green Chemistry. She has experience of12 yearsin Teaching and 15 years in research. She has 65 Research papers on her credit published in various National and International Reputed Journals. She also published 01 book with ISBN number. Attended various conference, seminar, workshops and FDP's delivered many lectures as a Resource Person. She has total citation-80, h-index-4, i10 index-3 on google scholar. She has conducted Career Oriented Course on "Water and Soil Analysis" sponsored by UGC New Delhi. Convener of 03 National Chemistry Conferences and 02 Faculty Development Programs. Working as Chairman of Criterion-VI for NAAC. She has awarded by Maulana Azad National Fellowship from UGC New Delhi. She has also awarded by National Best Researcher International Award-2021, Best Teacher of the Year National Award-2022, Best oral and poster presentation award and others. Working as an Editorial board/Reviewer of Int. J. of Pharmaceutical Sciences Review and Research,Pure and Applied Biosciences, Science PG publications, Excel Journal of Engineering Technology & Management Science, IJASTEMS, IJARMPS, life member of various journals. Working as secretary of Nandini Educational Society running two Aided Schools.

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