

**AN ANALYTICAL STUDY TO DETERMINE THE DETOXIFYING EFFECT OF
HARIDRA (*CURCUMA LONGA* LINN) ON IMIDACLOPRID RESIDUE IN BABYCORN
(*ZEA MAYS*)****Dr. Swathi M.*¹ and Dr. Ashwin Kumar S. Bharathi²**¹Assistant Professor, Department of Agada Tantra, Ashwini Ayurvedic Medical College and Hospital, Tumkur.²Professor and Head of the Department, Department of Agada Tantra, Sri Dharmasthala Manjunatheshwara College of Ayurveda & Hospital, Hassan.***Corresponding Author: Dr. Swathi M.**

Assistant Professor, Department of Agada Tantra, Ashwini Ayurvedic Medical College and Hospital, Tumkur.

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1. ABSTRACT

Background & Objectives: Pesticides are toxins designed to kill and in addition to killing of the pests may also pose potential harm for human health. Baby corns are one such vegetable where heavy unrestrained spraying of pesticides can be observed. There are indisputable evidences to illustrate the hazardous effects of the sprayed pesticides. Ayurveda has explained many detoxifying measures which can be wisely used to nullify the harmful effects of these toxins. Hence an attempt was made in this study to analyse the efficacy of *Haridra* in pesticide residue removal and to compare the pesticide residue after water wash and treatment with *Haridra jala* and *kashaya*. **Methods:** Samples of baby corns were collected were grouped into 5 equal parts. One part was kept as control and remaining four were applied with washing techniques by washing with tap water, salt solution, *haridra jala* and *haridra kashaya* respectively. These were then subjected to extraction and then injected in to Gas chromatography for evaluation of concentration of imidacloprid. **Results:** Significant reduction in the residual concentration of pesticides was observed in all the methods of washing. **Interpretation & Conclusion:** Washing with *haridra kashaya* was found more efficient method of washing compared to salt water which is cost effective and easily practicable.

KEYWORDS: baby corns; Pesticide residues; *Haridra*; Washing method; imidacloprid.**1. INTRODUCTION**

In modern times, the susceptibility of humans to pollutants is inevitable due to industrialisation and urbanisation. Contaminants have also certainly been released to nature. Pesticides are one of the most common exposed toxins in this class as it is used in various fields, such as agriculture, public health etc.

As the demand for food is increased, measures have to be taken to meet the ratio of demand and supply to minimise the loss of food during raising, processing and storing by pests. As a result of this, the synthetic pesticide was introduced with more success than the traditional pesticide process. As synthetic pesticide provided a promising effect over controlling pests, many agriculturists started using them injudiciously due to the ignorance or greed. This has led to increased pesticide residual level within the final agricultural production. Pesticides are used to protect food crops from pests whose residues are harmful to human and animal health.^[1] Their long term, low dose exposure is linked to the human health effects such as immune suppression, hormone disruption, diminished intelligence,

reproductive abnormalities and cancer.^[2] Failure to use will lead to growth of filamentous fungi mycotoxins.

Pesticide consumption in 2014-15 was 0.29kg/ha (GCA), which is roughly 50% higher than in 2009-10 and in Karnataka it was 1675tonnes in 2008-09 & 0.10per ha(kg) in 2016-17.^[3] Imidacloprid a neonicotinoid pesticide concentration was 22%, 24%, 33% of fruit, vegetable and cereal samples.^[4]

Karnataka is the second predominant state that contributes 16.5% of total maize production.^[5] Treating corn seeds with pesticides provide protection against early-season thrips and reduce yield loss under field conditions.^[6] Baby corns belong to the maize family and this cereal grain is harvested when they are small in size and immature. They are handpicked, and are usually pale yellow, blue pink to off white in colour depending on the variety, and has bland taste.^[7]

Imidacloprid a neonicotinoid pesticide, with active principles of nicotine is used in the most of fields and horticultural crops.^[8] This group comes under systemic

pesticide, and when applied; it is absorbed from sap and spread to all parts of plant including seed. It interferes with the transmission of stimuli in the insect's nervous system by causing a blockage in the nicotinic neuronal pathway. This pathway is more common in insects than in warm blooded animals, making the chemical more toxic to insects resulting in paralysis and the death of insects.^[8]

Small doses of these pesticides after long term usage causes cumulative toxicity effect on human beings. Ayurveda explains in detail about the cumulative toxicity symptom on human being and its treatment.

Agada tantra is the science which deals with toxic, combination of toxic and their treatment including *jangama*, *kritrima*, *stavara* and *dooshivisha*. *Dhathu visha*, *gara visha*, *viruddha ahara* is also dealt under *agada tantra*.

Acharya Charaka has explained *vishagna dashemani*, which has ten drugs in it and are useful in *visha* condition, one among them is *Haridra*, which is available easily used abundantly. *Haridra* has various pharmacological actions like anticancerous, hepatoprotective, nephroprotective activity etc.^[9] As it is the main spice used in every household, it is helpful to reduce the pesticide residue from baby corn. The common method of washing vegetables are normal water and salt water, but in this study *haridra jala* was used to wash baby corns with different concentration and reduction of activity and pesticide residue level were analysed.

There are many instruments to measure the pesticide residue level, among them gas chromatography gives the results which are more accurate and reliable both qualitatively and quantitatively.

2. HYPOTHESIS

H₀. There is no effect of *Haridra jala* and *Haridra kashaya* in removing pesticide residue from baby corns.

H₁. *Haridra jala* and *Haridra kashaya* has got significant effect in removing pesticide residue from baby corns.

3. MATERIALS AND METHOD

- Source of sample: Baby corn was collected from the local market.
- Source of test drug: Organic haridra was collected from cultivators
- Source of standard: Imidacloprid standard suitable for GCMS is bought from Sigma Aldrich

4. RESULTS

Sample	Retention time(min)	Area	Imidacloprid conc(ppm)	% inhibition	Chromatogram Ref
Imidacloprid standard	18.183	22101749	100	-	Fig. 1
Sample A- unwashed	18.103	7238492	3.28	-	Fig. 2
Sample B- tap water	18.083	5032693	2.28	30.48	Fig. 3
Sample C- salt water	18.111	5010793	2.27	30.79	Fig. 4

- Quantification of Imidacloprid in Baby Corn
 - Test samples:
 - i. Baby corns-unwashed
 - ii. Baby corns washed in tap water
 - iii. Baby corns washed in 2% Salt solution
 - iv. Baby corns washed with Aq Haridra extract (24% w/v)
 - v. Baby corns washed with concentrated Aq Haridra concentrate
 - Imidacloprid analysis by GCMS
 - Extraction of Imidacloprid from baby corn:
 1. Baby corn samples (10g) were homogenized in 50 ml water in mortar and pezzle.
 2. The homogenate was sonicated in an ultrasonic bath for 15min.
 3. The homogenate was filtered through Whatmann Filter paper No. 1.
 4. Filtrate (25mL) was taken in a separating funnel and Imidacloprid was partitioned thrice with chloroform 5mL.
 5. The lower chloroform layer was passed through anhydrous sodium sulfate.
 6. The chloroform was evaporated to dryness under reduced pressure and reconstituted in 1ml of Chloroform.
 7. Similar kind of procedure is followed in all the test sample groups.
 - Imidacloprid Standard: Bayer pesticide formulation (17.5% W/V) was used as standard. A master stock of 100ug/mL in acetonitrile was prepared and used for analysis.
 - GCMS analysis:
 1. Gas chromatograph—QP2010 Shimadzu GCMS/MS
 2. GC column: RdX -5, 30m x 0.25mm, 0.25µm
 3. Head column pressure 105 kPa
 4. Injection mode: 10µL Split mode
 5. Injector temperature 250 °C
 6. Injected volume 2µL
 - Oven programme
 1. 60° C (2min), 10° C per min 60 to 300
 2. 300 °C (5 min)
- Imidacloprid was quantified using formula:

$$\text{Imidacloprid } (\mu\text{g/g}) = \frac{\text{Sample Area}}{\text{Standard Area}} \times \text{Std concentration} \times \text{Dilution factor}$$

Sample D- <i>haridrajala</i>	18.100	4285357	1.94	40.85	Fig. 5
Sample E- <i>haridrakashaya</i>	18.125	3863547	1.75	46.64	Fig. 6

The first sample - Sigma standard of the Imidacloprid which is in its pure form, hence the concentration of 100ppm, which is further used to identify the compound for analysis of the samples.

Second sample - *Zea mays* which is collected from the local market and subjected to the analysis of residue level of pesticide in the sample which showed the results as 3.28ppm which is exorbitantly high when compared to the WHO standard of acceptable daily limit of 1 µg/kg.

Third sample- *zea mays* after washing with the potable water it showed 30.48% inhibition of residue level which brought the residue to the 2.28ppm.

Fourth sample- analysed in the GCMS, of *Zea mays* washed with salt water which showed the reduction upto 30.79 % which reduced the residue to 2.27ppm.

Fifth sample- is of the *Zea mays* washed with *haridra jala* which reduced the residue by 40.85% which brought down the residue to 1.94ppm.

Sixth sample- the *Zea mays* washed with *haridra kashaya* solution showed the highest result in the reduction of the pesticide by 46.64% which brought down the residual value to 1.75ppm.

5. DISCUSSION

Pesticides are the chemical products used for plant protection. They include Insecticides, Fungicides, Herbicides and plant growth regulators. Residues of pesticides may remain in treated products and get into human food chain. These residues are monitored for a safe permissible value and should not exceed a limit above which they may pose risks to human health. The concepts of Maximum Residue Limits (MRLs), Acceptable Daily Intake (ADI) and Theoretical Maximum Daily Intake (TMDI) for pesticides have been devised to keep a check on the pesticides' residues in the food chain and keep them within the safe limits.

The ever rising needs for the agricultural products and maximum profit has forced the farmers to use these pesticides far beyond the permissible limit. The reports from the Ministry of Agriculture & Farmers Welfare say that almost all vegetables are available in the market are in an unrestrained manner.

Neonicotinoids are systemic pesticides which are currently used in agriculture and for industrial pest control. Imidacloprid is a neonicotinoids which is a derivative of nicotine. They have the capacity to enter the plant through the soil or leaves and spread throughout the stem, leaves, fruits, and flowers. The pesticides enter into nervous system of insects which chew or suck the pesticide treated plants and ultimately they die. The same residues present on plant tissues when consumed by humans in small dose for longer duration can get accumulated leading to chronic nicotine poisoning.

Ayurveda grantha's have mentioned the guidelines for preparation, use and consumption of food under *Ashta ahara vidhi visheshaaayatana*. It also conveys *toya agni samskara* (contact with water and fire) and *shoucha* (purification) procedures. The main aim of *samskara's* (to refine) is either to fetch the changes in properties or remove the toxic principles or detoxifies the chemicals by means of washing or processing with antitoxic herbs. On the basis of these principles an attempt was made to purify baby corns in different methods viz. washing with water, salt water, *Haridra jala* and *haridra kashaya*. *Haridra* is mentioned among *vishaghna dashemani* and they should have the potency to detoxify baby corns from the induced artificial toxins in the form of pesticides.

6.1 Discussion on the materials included under the study

Pesticides

Imidacloprid is a neonicotinoids which is a derivative of nicotine. They have the capacity to enter the plant through the soil or leaves and spread throughout the stem, leaves, fruit, and flowers. The pesticides enter into nervous system of insects which chew or suck the pesticide treated plants and ultimately they die. The same residues present on plant tissues when consumed by humans in small dose for longer duration can get accumulated leading to chronic nicotine poisoning.

The residues of this pesticide have the capacity to mix with soil and it gets broken down to different chemicals easily by water and sunlight. The rate of imidacloprid breakdown is affected by the pH and temperature of the water depending on which bonds in the molecules are broken. Some metabolites are more toxic than the parent compound. Under some circumstances, imidacloprid can leach from the soil into groundwater.

For example, Desnitro - imidacloprid, has a high affinity for mammalian nAChRs and is considered to be extremely toxic to mice (chao and casida 1997). It is produced in a mammalian's body during metabolism or in the atmosphere (koshlukova 2006).

Imidacloprid is one of the most dangerous pesticides for the environment and humans. There is a need for minimizing the exposure and hence this study was initiated to find the efficient way.

Baby corns

Zea mays commonly known as corn or maize are commonest cereals of many households in India. It is used in the form of corns, flour, starch, syrup etc. As demand for supply increases the production also increases. To prevent the loss during the production and storage due to pests, imidacloprid are used. These when

consumed or exposed regularly causes rapid accumulation causing toxic effect on humans.

Observing the toxic effects, it was essential to use Zea mays for determining the power of haridra on imidacloprid residue levels.

Tap water

On daily basis, Fresh fruits and vegetables are often washed with tap water to remove dirty marks on the surface, which are then consumed directly. However, tap water has a limited effect on the removal of pesticide residues, because many pesticides are hydrophobic.^[10]

Salt water

As there is a limited effect of removing residues by washing in normal tap water, it is replaced by salt water. Salt water [sodium chloride (NaCl) solution] is largely used to decontaminate the pesticide residues from different fruits and vegetables. Studies have proved effective in removing pesticide residues from fruits and vegetables.^[11]

While plain tap water washing have not shown any promising effect in the removal of residues below MRL levels, washing with 2% salt water yielded very good effect in the removal of the residues below MRL levels.^[12]

Haridra

Vishaghnadashemani explained in *Charaka samhitha sutra sthana* contains *Haridra*, *manjishtha*, *suvaha*, *sukshmaela*, *palindi*, *chandana*, *kathaka*, *shirisha*, *sinduvara*, and *shleshmataka*. These drugs can be used as primary drug or combination drug to detoxify the poison. Depending on the drug's availability or the need it can be opted.

Haridra is botanically known as *Curcuma longa* has a wide variety of pharmacological properties, including anti-diabetic, anti-allergic, anti-cancer, antiseptic, antioxidant, and so on. *Haridra* is one of the most widely used spices, readily accessible and affordable and used as first aid and for minor injuries in many parts of India. *Haridra* has proven to have binding properties with metals and non-metallic compounds and its adsorption properties helps in pulling out the pesticide residues towards it. This property can be made use to remove the pesticide residue from these vegetables.

6.2 Discussion based on the observed results

The efficacy in removal of pesticide residue in baby corns by the different methods proposed here are to be analysed. The test sample included 3.28 ppm of imidacloprid, although the WHO's daily recommended limit for imidacloprid is 1ppm.

The untreated Zea mays sample was first evaluated, yielding a value of 3.28ppm, which is regarded to be 100 per cent. Then the first test solution, Zea mays rinsed

with portable water and analysed, yielding a pesticide residue 30.48 per cent inhibition. The second test solution was 2 per cent salt solution, which had 30.79 per cent inhibition. The third test solution was 2.4 percent *haridra jala*, which had 40.85 per cent inhibition. The final test solution was *haridra kashaya*, which yielded 46.64 per cent inhibition.

6.3 Probable mode of action

Probable mode of action may be

1. Hydrolysis
2. Osmosis

Hydrolysis^[13]

Water degrades pesticides by dividing large molecules into smaller ones, breaking them down in the process called hydrolysis. Hydrolysis of pesticides can occur on the soil surface, in the root zone, or whenever a source of water is available. Hydrolysis may be very active in warm water at or near the soil surface. As the water temperature cools at depths below the root zone, the rate of hydrolysis slows. In deep groundwater, hydrolysis slows dramatically.

- Imidacloprid is stable to hydrolysis in acidic or neutral conditions, but hydrolysis increases with increasing alkaline pH and temperature.
- Researchers determined that hydrolysis of imidacloprid produced the metabolite 1-[(6-chloro-3-pyridinyl) methyl]-2-imidazolidone. This may be further broken down via oxidative cleavage of the N-C bond between the pyridine and imidazolidine rings, and the resulting compounds may be broken down into CO₂, NO₃⁻, and Cl⁻.
- When imidacloprid was added to water at pH 7 and irradiated with a xenon lamp, half of the imidacloprid was photolyzed within 57 minutes.
- At pH 7, only 1.5% of the initial concentration of 20 mg/L of imidacloprid was lost due to hydrolysis in three months, whereas at pH 9, 20% had been hydrolyzed in samples that were kept in darkness for the same time period.^[14]
- ❖ pH of normal water and salt solution may vary from 6.5 – 8. The pH of turmeric may have the range between 7.4- 9.2.^[15]
- ❖ When the pH is more alkaline the hydrolysis of imidacloprid also increases. When the result was analysed *haridra kashaya* was more effective than salt water and normal water.

Osmosis

Osmosis is a process in which solvent molecules prefer to pass through a semipermeable membrane as they move from a lower concentration to a higher concentration. As a result, the solvent from the solution may have gone through the baby corn, diluting the imidacloprid concentration and assisting in the reduction of residue.

Haridra a vishaghna dravya is said to be efficient in detoxifying the poisons. Pesticides are in fact poisons

which can be considered as *garavisha*. Moreover turmeric has been proved to have many antitoxic properties.

The media used in the process of *Shodhana* has very important role in either breaking down or destroying the chemical constituent that is not required. The heat treatment - constant boiling of the drug in a particular media for a particular duration has a role in the modification of the chemical constituents etc.^[16]

The chemical constituents in turmeric may be effective in denaturing the poisonous pesticides and making it harmless or it may help in breaking the adhesion of the pesticides so that they can be washed off easily.

Boiled *Haridra* water has more significantly reduced the concentrations of pesticide than normal water wash and salt water wash. Possibly, either oxidization or hydrolysis and the chemical constituents of the turmeric have caused the degradation of pesticide by chemical reaction, which might have formed a stable compound which was washed off easily by water.

6. CONCLUSION

Corns are the commonest cereal which may be used in the different forms contains neonicotinoid named imidacloprid. The proportions of pesticides being sprayed is far above the MRL set up by the regulatory bodies. This results in the intake of a substantially large amount of pesticide in to our body leading to various toxic effects. Washing with plain water is effective in removing these pesticides superficially since they bind a portion of the pesticides within. So as an effective measure to remove these, washing with salt water, *Haridra jala* and *haridra kashaya* would be beneficial.

The percent inhibition of tap water wash was 30.48 per cent, salt water was 30.79 per cent, *haridra jala* was 40.85 per cent and *haridra kashaya* 46.64 per cent. *Haridra kashaya* removes the pesticides with a significant result when compared to salt water. Though there is slight difference between water wash, salt water, *Haridra jala* and *Haridra kashaya*, the removal of the pesticide residue even in a small per cent is blessing for the body. So it can be concluded that washing of baby corns bought from the market which had pesticides can be easily detoxified to a considerable amount by using *Haridra kashaya*, which is cost effective and easily practiced. And hence based on the observations, the null hypothesis can be rejected and the alternate hypothesis can be accepted. Ie

H1 - *Haridra jala* and *haridra kashaya* has got significant effect in removing pesticide residue from baby corns.

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