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Process Development of Pesticide Production from Azadirachta Indica A. Juss.

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Abstract **- The Neem tree (*Azadirachta indica A. Juss*.) has been known as the wonder tree for centuries in the Indian subcontinent as it offers answers to some of the major concerns facing humankind. Its mammalian safety and environmental friendliness reports are highly encouraging. A key advantage to using Neem, as opposed to some medical treatments and other herbs, is its harmlessness on human health. Millions have been using Neem over thousands of years and no hazards have been documented for normal dosages. The general class of these compounds found in neem is triterpenes, within which, the most effective are the limonoids, which are abundant in Neem oil. Azadirachtin, a limonoid, has been found to be the main ingredient for fighting insects and pests, being up to 90% effective in most instances. It repels and disrupts the life cycle, however does not kill immediately, but is nonetheless is one of the most effective growth and feeding deterrents ever examined. Meliantriol is another feeding inhibitor, which prevents locusts chewing, and has therefore been in traditional use in India for crop protection. In this , we develop two batch processes for neem pesticide production, water- based neem leaf extract and neem oil based pesticide. The former can be sprayed directly on the infestation, while the latter can be diluted to the concentration needed, according to the degree of infestation on the plant. For the oil-based pesticide, we study the kinetics and thermodynamics pertinent to the extraction process, thus to prove that the extraction process carried out is a feasible one.**

Keywords **– Azadirachtin, limonoid, Meliantriol, Neem.**

I. INTRODUCTION

Medicinal plants are part of human society and are used to combat diseases, not only those of animals but of plants as well, from the dawn of civilization. *Azadirachta indica A. Juss* (syn. *Melia Azadirachta*) is well known in India and its neighboring countries for more than 2000 years as one of the most versatile medicinal plants having a wide spectrum of biological activity. *A. indica A. Juss* and *M. azedarach* are two closely related species of Meliaceae. The former is popularly known as Indian neem (*Margosa tree*) or Indian lilac, and the latter as the Persian lilac. Neem is an evergreen tree, cultivated in various parts of the Indian subcontinent.

Every part of the tree has been used as traditional medicine for household remedy against various human ailments, from antiquity. Neem has been extensively used in ayurveda, unani and homoeopathic medicine and has become a cynosure of modern medicine. The Sanskrit name of the neem tree is *'Arishtha'* meaning *'reliever of sickness'* and hence is considered as *'Sarbaroganibarini'*. The tree is still regarded as *'village dispensary'* in India.

The importance of the neem tree has been recognized by the US National Academy of Sciences, which published a report in 1992 entitled 'Neem – a tree for solving global problems'. The neem tree has been described as *A. indica* early in 1830 by De Jussieu

II. CHEMICAL COMPOUNDS IN NEEM

Chemical investigation on the products of the neem tree was undertaken extensively in the middle of the twentieth century. In 1942, *nimbin*, the first bitter compound was isolated from neem oil. Since then more than 135 compounds have been isolated from different parts of neem and several reviews have been published on the chemistry and structural diversity of these compounds.
The compounds have been divided into two major classes:
A. Isoprenoids and others - These include diterpenoids and triterpenoids containing protomeliacins, limonoids, azadirone and its derivatives, gedunin and its derivatives, vilasinin type of compounds and Csecomeliacins such as nimbin, salanin and azadirachtin.
B. Nonisoprenoids - These include proteins (amino acids) and carbohydrates (polysaccharides), sulphurous compounds, polyphenolics such as flavonoids and their glycosides, dihydrochalcone, coumarin and tannins, aliphatic compounds, etc.

The chemical formulae of some of the compound isolations from neem are listed below:

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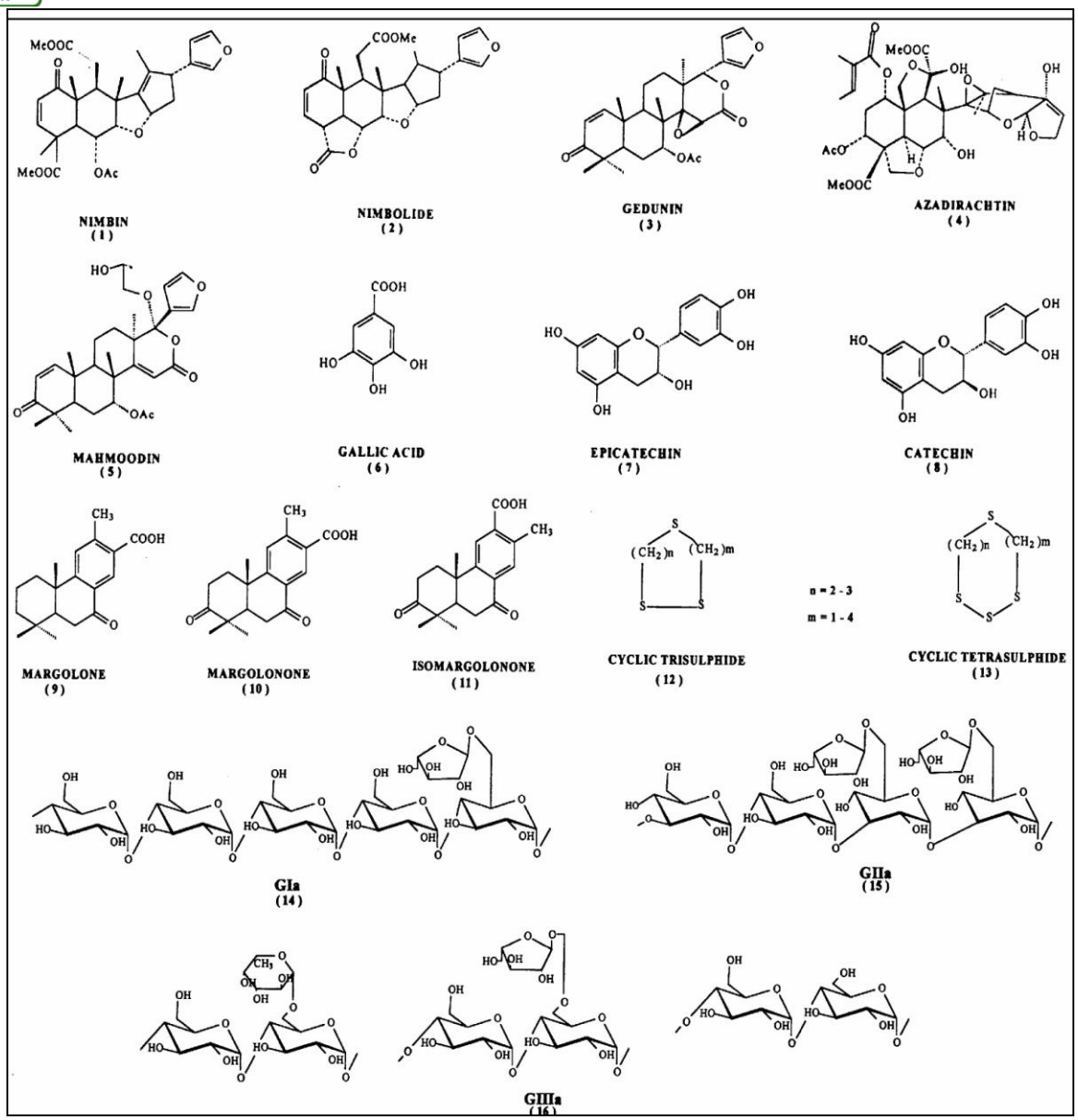

Fig.1. Chemical Compounds in Neem

III. EXPERIMENTAL WORK

The experimental work was carried out in two parts. The first stage was the production of neem leaf extract and the second was extraction of oil from neem seed kernels, which was further processed to fabricate the pesticide.

The produced pesticides were used on plants having insect infestations. The subject plants were studied for a certain period to study the effect and efficiency of produced pesticides.

A. Production of Neem leaf extract

Neem leaf extract is nothing but a water based extract, containing azadirachtin and other chemicals, which are responsible for the pesticidal properties.

For preparing the neem leaf extract, a domestic approach was considered.

- About 250 grams of neem leaves were taken. The leaves were washed thoroughly with water to remove dirt collection on the leaf surface.
- Once the leaves were dried, they were ground in a grinder with one-liter water.
- The solution thus obtained was kept for about a week and was stirred occasionally during the period. This is done so that the chemicals from the leaves mix well with water.
- The liquid was filtered with a cloth, because of which the neem bulk was separated from the solution, and a finer liquid was obtained, which contained fine particles of neem leaves. This was named first filtrate.
- The liquid thus obtained was filtered again, for the second time, with a finer filter medium, a filter paper.
- This provided a clear filtrate, without any clouding, which was the final leaf extract.The obtained cake was dried. This cake can be used for various domestic purposes or as an additive to fertilizers.

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Fig.2. Neem Leaf Extract

B. Effect of Neem leaf extract on subject

- The produced neem leaf extract shown in the above image was further put to test to study its effect and efficiency on an infested plant.
- The subject plant chosen for this experiment was a curry-leaf plant [*Murraya koenigii*]. The subject was observed to be infested with white, small, scaly, plant chewing insects.
- The extract was sprayed directly, without dilution with water or any other solvent, on the shrub continuously for four days, two times a day.
- By the third day, an appreciable diminution in the infestation could be observed on the plant, proving the positive effect of the extract.


Fig.3. Effect of leaf extract

C. Oil Extraction

- The neem seeds contain kernels, which are processed to extract oil. Kernels can contain up to 45% (by weight) of oil. The following is the experimental work that was carried out for the extraction of neem oil.About 250 grams of neem seeds were taken and washed thoroughly with water to remove any dirt accumulation
- Dried seeds were dried in sun for about a week, after which they were ground in a grinder to an approximate size of 0.5 mm - 1 mm
- The ground powder was added to hexane, stirred thoroughly and left undisturbed for three hours
- The arrangement was filtered to obtain a clear hexane-oil solution
- This solution was distilled to obtain a hexane free oil yield.

D. Oil-based pesticide production

The goal was to prepare a water-soluble pesticide that can be diluted as per the need and as per the infestation to the plant on which it is supposed to be used. Hence, the obtained oil was further processed to obtain a water-soluble pesticide, which can be diluted as per need. For this, the obtained oil was mixed with liquid detergent and water in a ratio of 15:5:7

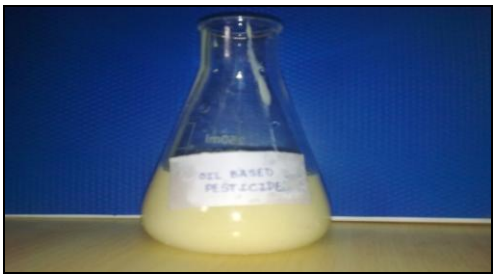
Fig.4. Oil based pesticide

E. Effect of oil based pesticide on subject

- The produced neem oil-based pesticide was put to test to find out its efficiency. The subject chosen for this experiment was a rose plant infested with white flaky insects.
- The oil-based pesticide was diluted with water in a 1:5 ratio
- The obtained dilution was sprayed on the infested subject two times a day each day
- By the third day the infestation was observed to be reducing and by the fourth day a significant reduction in the white colonies was observed

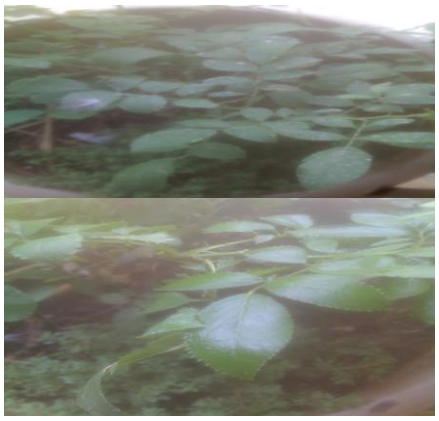
Fig.5. Effect of Oil-based pesticide

IV. PROCESS DEVELOPMENT

As we are treating the production of pesticides from neem in the form of leaf extract and from the oil obtained from neem seed kernels, the following processes for their batch wise production are proposed.

A. Neem leaf extract

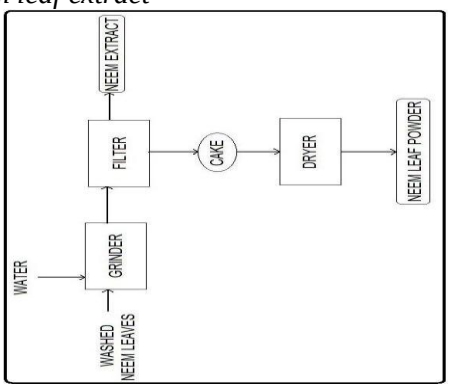

Fig.6. Batch process for Neem leaf extracts production

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B. Process escription

A batch process for production of neem leaf extract was developed. As the starting step, neem leaves are separated from the tree and are washed thoroughly with water. This step is necessary to remove any dirt or other undesirable accumulations on the leaves, which may reduce the efficiency of the final product or may harm the equipments in the process. The washed neem leaves are then sent to the next operation, which is grinding. Here, water is added to the leaves in the grinder, and the leaves are ground. Amount of water is kept such that the solution formed is free flowing and not a semi-solid paste. This liquid is then passed on to the next operation, which is filtering. The filter filters the solution, to give a clear solution and a cake is obtained as the side product. The filtered solution, in case of cloudiness, can be filtered furthermore to obtain a clear, brown liquid, known as neem leaf extract.

The obtained cake can be further processed for usage in a variety of agricultural and domestic applications. The processes include drying the cake, to obtain a dry neem leaf powder. Otherwise, one can use it readily as an additive to manures or solitarily for mulching.

C. Oil-based pesticide

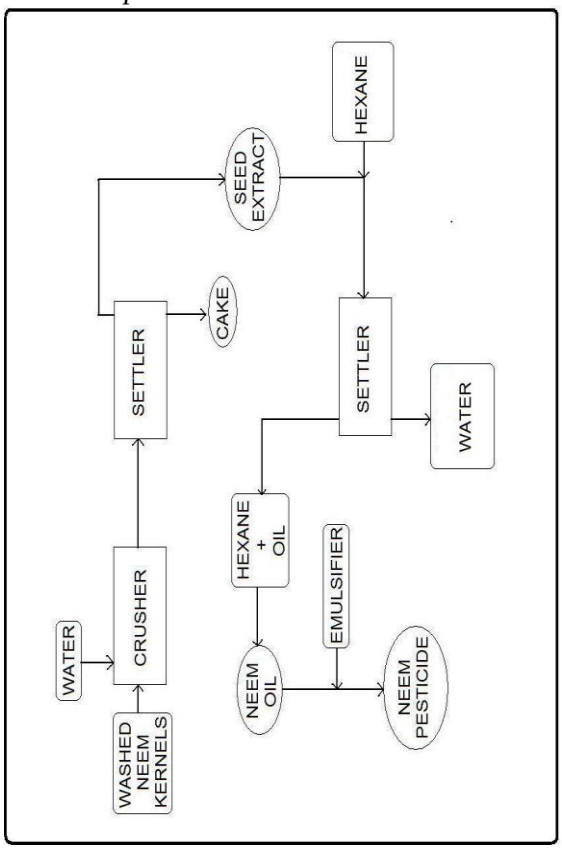

Fig.7. Batch process for Neem oil-based pesticide production

V. Process Description

The second process developed for production of pesticides was that of oil-based pesticide containing an emulsifying agent such as detergent so that a dilutable concentrate is obtained.

The production process starts with thorough washing of neem seeds with water. This step ensures removal of dirt on the seeds, which may reduce the effect of the final product of the process. After having washed, the seeds are dried in a dryer until the moisture content in the seeds in reduced significantly. The dried seeds are then sent to a crusher, where the seeds are crushed with water. The product of this certain operation should be free flowing, and the amount of water fed is decided accordingly. The obtained liquid is then sent to a settler, where it is left to settle undisturbed for a certain amount of time. After having left for some time, the bulk settles as the bottom layer and the liquid settles as the top layer. The bottom settlement can be separated out as the cake, and can be processed for further use. The separated cake may contain significant amounts of oil still left in it, which can be separated by leaching again.

The liquid that is separated as the top layer is sent to the next step, the solvent extraction. A polar organic liquid such as hexane is chosen for extraction, in which oil is readily soluble but water is not. As a result, water is separated out, and a hexane-oil solution is obtained. Simple distillation can be carried out with this solution to evaporate the hexane content in the solution, and hence to obtain solvent-free oil as the product. In this way, a solvent free oil yield is obtained. This oil needs to be blended with an emulsifying agent, so that a surfactant-based oil pesticide is obtained which can be diluted with water. The emulsifying agent can be detergent or liquid soap added in a certain fixed ration to obtain the final product.

VI. Result and Discussion

As for the calculations of the neem pesticide production, the mass balances, the kinetics and the thermodynamics of the process were studied.

A. Mass balance for Neem leaf extraction

Neem leaves = 250 g

Neem Solution (Leaves + water)

$x = 1\ l$

First Extract = $y = 0.8\ l$

Cake Formed = z

Second Extract = $a = 0.650\ l$

Fine Cake = b

Total cake obtained = d

Overall Material Balance

$x = y + z$

➔ $1 = 0.8 + z$

➔ $z = 0.2l$

Material Balance for Second Filtration

$y = a + b$

➔ $0.8 = 0.650 + b$

➔ $b = 0.150l$

Hence total cake obtained;

$d = z + b$

➔ $d = 0.2 + 0.150$

➔ $d = 0.350l$

Hence from a $1l$ solution, on filtration the total leaf extract obtained was $0.650\ l$ and the cake obtained was $0.350l$.

B. Thermodynamics of the extraction process

Thermodynamics parameters (ΔH, ΔS and ΔG) for the extraction of neem oil using n-hexane and ethanol as solvents can be estimated using following equations,

$$\ln K = -\frac{\Delta G}{R}\frac{1}{T} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R}$$

$$K = \frac{Y_T}{Y_u} = \frac{m_L}{m_S}$$

Where,

K is equilibrium constant

Y_T is yield percent of oil at temperature T

Y_u is percent of oil remaining in Neem seed

m_L is amount of Neem oil in liquid at equilibrium temperature T

m_S is amount of Neem oil in solid at equilibrium temperature T

R is gas constant,

$H\Delta$, $S\Delta$, and $G\Delta$ are enthalpy, entropy, and free energy of extraction, respectively

The values of K and for extraction of Neem oil using n-hexane and ethanol as solvents were calculated using Eqs. (1) and (2). These values are summarized in the tables that follow.

Table 1

Temperature	***K***
303 K	2.96
313 K	4

Using the values for K, the values for ΔG can be calculated using the equations given above

Table .2

Temperature	K	ΔG
303	2.96	-2733.74
313	4	-3492.27

The values of ΔH ΔS can be calculated as well

Table 3

Temperature	K	ΔH	ΔS
303 K	2.96 J/mol	2650.26 J/mol	17.76 J/mol

The values of enthalpy and entropy of extraction are given in Table 3.

The negative values of ΔG indicate that the extraction of Neem oil using n-hexane and ethanol are spontaneous process. The positive value of enthalpy indicates that the process is endothermic and requires energy during process.

VII. Conclusion

The produced pesticides neem leaf extract and oil-based pesticide were sprayed on pest-infested subjects and the following results were obtained.

- The Neem leaf extract showed significant reduction in pest infestation in a period of seven days
- The oil-based pesticide showed reduction in pest infestation in four days time

Hence we can conclude that the oil-based pesticide is more efficient in pest control than the neem leaf extract.

The maximum yield obtained from extraction of neem oil was 32% for n-hexane at 50°C and 0.5 - 1mm particle size. This extraction follows first order kinetic with smaller value as decrease of temperature. It also found that ΔH is positive, ΔS is positive, and ΔG is negative indicating that this process is endothermic, irreversible, and spontaneous.

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