

Review Concept of Application of Differential Equations

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Abstract: This article attempts the basic concepts of Differential equations and studies one of the application of Differential equations which is Newton's law of cooling. It gives the derivation of this and explains its role in Engineering connection. It solves some problems related to this.

Keywords: Differential equation, heat flow, Newton's law of cooling

1. INTRODUCTION:

One physical system in which many important phenomena occur is that where an initial uneven temperature distribution causes heat to flow. As heat flows the temperature distribution changes, which modifies the heat flow. That is heat flows from hot places to cold ones, and as this happens the temperature of the cold places rises and the temperature of hot places decreases.

There are two rough mathematical rules governing the relation between heat flow and temperature change. Heat flow is proportional to rates of change in temperature distribution. The time of temperature change at any point is proportional to the rate of heat flow into that point

2. PRELIMINARIES AND BASICS:

2.1 Definition: A differential equation is an equation that relates an unknown function and one or more of its

derivatives of with respect to one or more independent variables. For instance, the equation $\frac{dy}{dx} = -5x$ relates the first derivative of y with respect to x , with x . Here x is the independent variable and y is the unknown function (dependent variable).

If $\frac{d^n y}{dx^n}$ is the n -th derivative of y with respect to x . One can also use the notation $y^{(n)}$ to denote $\frac{d^n y}{dx^n}$. It is further convenient to write $y' = y^{(1)}$ and $y'' = y^{(2)}$. In physics, the notation involving dots is also common, such that \dot{y} denotes the first-order derivative.

Different classifications of differential equations are possible and such classifications make the analysis of the equations more systematic.

2.2 Classification of Differential Equations

There are various classifications for differential equations. Such classifications provide remarkably simple ways of finding the solutions (if they exist) for a differential equation. Differential equations can be of the following classes.

2.2.1 Ordinary Differential Equations

If the unknown function depends only on a single independent variable, such a differential equation is ordinary.

$$L \frac{d^2}{dt^2} Q(t) + R \frac{d}{dt} Q(t) + \frac{1}{C} Q(t) = E(t),$$

The following is an ordinary differential equation: , which is an equation which arises in electrical circuits. Here, the independent variable is t .

2.2.2 Partial Differential Equations

If the unknown function depends on more than one independent variables, such a differential equation is said to

$$\alpha^2 \frac{\partial^2}{\partial x^2} f(x, t) = \frac{\partial}{\partial t} f(x, t)$$

be partial. Heat equation is an example for partial differential equations:
t are independent variables.

Here x,

2.2.3 Homogeneous Differential Equations

If a differential equation involves terms all of which contain the unknown function itself, or the derivatives of the unknown function, such an equation is homogeneous. Otherwise, it is non-homogeneous.

2.2.4 N-th order Differential Equations

The order of an ordinary differential equation is the order of the highest derivative that appears in the equation. For example $2y''(x) + 3y'(x) = 5$, is a second-order equation.

2.2.5 Linear Differential Equations

A very important class of differential equations are linear differential equations. A differential equation $F(y, y'(x), y''(x), \dots, y^{(n)}(x)) = g(x)$ is said to be linear if F is a linear function of the variables $y, y'(x), y''(x), \dots, y^{(n)}(x)$

2.3 Note: If a differential equation is not linear, it is said to be non-linear.

2.4 Solutions of Differential equations

2.4.1 Definition

To say that $y = g(x)$ is an explicit solution of a differential equation $F(x, y, dy/dx, d^2y/dx^2, \dots, d^ny/dx^n) = 0$ on an interval $I \subset \mathbb{R}$, means that $F(x, g(x), dg(x)/dx, \dots, d^ng(x)/dx^n) = 0$, for every choice of x in the interval I.

2.4.2 Definition

We say that the relation $G(x, y) = 0$ is an implicit solution of a differential equation $F(x, y, dy/dx, d^2y/dx^2, \dots, d^ny/dx^n) = 0$ if for all $y = g(x)$ such that $G(x, g(x)) = 0$, $g(x)$ is an explicit solution to the differential equation on I.

2.4.3 Definition

An n-th parameter family of functions defined on some interval I by the relation $h(x, y, c_1, \dots, c_n) = 0$, is called a general solution of the differential equation if any explicit solution is a member of the family. Each element of the general solution is a particular solution.

2.4.4 Definition

A particular solution is imposed by supplementary conditions that accompany the differential equations. If all supplementary conditions relate to a single point, then the condition is called an initial condition. If the conditions are to be satisfied by two or more points, they are called boundary conditions. Recall that in class we used the falling object example to see that without a characterization of the initial condition (initial velocity of the falling object), there exist infinitely many solutions. Hence, the initial condition leads to a particular solution, whereas the absence of an initial condition leads to a general solution.

2.4.5 Definition

A differential equation together with an initial condition (boundary conditions) is called an initial value problem (boundary value problem).

2.5 Basic definitions

- Order: Highest Derivative present in the differential equation
- Degree: Power of the higher derivative after free from radicals and fractions
- Formation of Differential Equation:
 1. Consider the given equation $f(x, y, a, b, c, \dots, d) = 0$
 2. Observe the no. of arbitrary constants if it is 'n'
 3. Based on Arbitrary constants differentiate the given Equation n times
 4. Using the n+1 equations including the given equation We get a differential equation of nth order.
- The standard form of First order linear differential equation is of the form $\frac{dy}{dx} = f(x, y)$

Homogeneous Function: A function $f(x,y)$ which satisfies the condition that

$$f(kx, ky) = k^n f(x, y)$$

A differential equation is said to be Homogeneous if the $f(x, y)$ is homogeneous of degree zero

For Homogeneous use $y = vx$ or $x = vy$ substitution based on the equation

For Non-Homogeneous in the case of $\frac{a_1}{a_2} = \frac{b_1}{b_2}$ use $ax+by=t$ as substitution and in the case of

$$\frac{a_1}{a_2} \neq \frac{b_1}{b_2} \text{ take } x = X + h \text{ and } y = Y + k \text{ as substitution}$$

- The necessary and sufficient condition for the differential equation

$$M(x,y)dx+N(x,y)dy=0 \text{ to be exact is } \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

The solution of the exact differential equation is $\int Mdx + \int Ndy = c$, under the first integral y constant and under the second integral terms do not contain x

The equation is not an exact differential equation if $\frac{\partial M}{\partial y} \neq \frac{\partial N}{\partial x}$ and it can be solved by applying various conditions like homogeneous, inspection, functions in xy , function of x alone, function of y alone and powers of x,y

- The standard form of First order linear differential equation is of the form $\frac{dy}{dx} = f(x, y)$

The linear differential equation of first order and first degree of Leibnitz is of the form

$$\frac{dy}{dx} + P(x)y = Q(x)$$

- The solution of the Leibnitz linear differential equation is $y(I.F) = \int Q(x)(I.F)dx + c$
- The Bernoulli's differential equation is of the form $\frac{dy}{dx} + P(x)y = Q(x)y^n$
To find the solution of Bernoulli's use the substitution as $y^{1-n} = t$

2. Newton's Law of Cooling:

It states that the rate of change of temperature of a body is directly

proportional to the difference between temperature of a body and its surrounding

medium. i.e $dT/dt \propto (T - T_s)$

the Newton's Law of Cooling is given by

$$dT/dt = k (T - T_s)$$

Where T_t is the temperature at time t and

T_s is the temperature of the surrounding,

k is a constant.

The Newton's Law of Cooling Formula is given by

$$T(t) = T_s + (T_0 - T_s) e^{-kt}$$

Where t is the time taken,

$T(t)$ is the temperature of the given body at time t ,

T_s is the surrounding temperature,

T_0 is the initial temperature of the body,

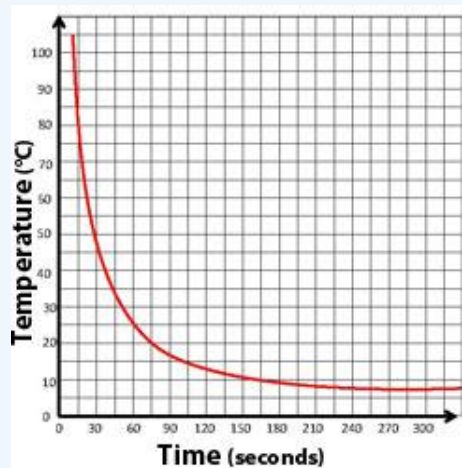
k is the constant.

NOTE: The greater the difference in temperature between the system and surrounding, more quickly the body temperature changes.

3. Engineering Connection:

Heat transfer is a broad topic used in many branches of engineering. For example, mechanical engineers who design engines from steam locomotives to modern internal combustion engines on a detailed understanding of how heat moves through all types of matter. Industrial engineers use heat transfer concepts to design climate control systems for manufacturing facilities, such as foundries or refrigerated food production facilities, which integrate temperature-sensitive human workers with extreme temperature processes. Moreover, heat transfer is so critical to biological engineering that it has spawned the specialty of "bioheat" transfer, which is the study of normal functioning of the cardiovascular system as well as inherently heated treatments such as cryo-surgery and laser-based therapies.

For example, If you placed a room-temperature can of soda in the refrigerator and waited for it to cool, its temperature change with respect to time is given by



4. PROBLEMS

Problem 1

A thermometer which has been at 70 F inside a house is placed outside where the air is at 10 F. 3 min later it is found that thermometer is at 25 F. Find the thermometer reading after 6 minutes?

Problem 2

A cup with water at 45 °C is placed in the cooler held at 5°C. If after 2 min the water temperature is 25 °C, when will the water temperature be 15° C?

Problem 3

A hard boiled egg at temperature 100° C is placed in 15° C water to cool. 5 Minutes later the temp of egg is 55° C. When will the egg be 25 °C?

5. CONCLUSION:

This article explains one of the application of Differential equations which is "Newton's law of cooling". It gives the derivation of this and explains its role in the engineering connection. It solves some problems by using this.

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Socio-economic aspects of people and Mangroves vegetation utilization in mudflat based villages of Krishna district

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Abstract: Mangroves are highly productive ecosystems with important economic and environmental functions. Based on vegetation status on three mudflat based villages the present study is to identify the species wise utilization and social-economic aspects among three villages i.e, Interu, Kruthivenu and Nidamaru. The socio-economic situation and resource utilization among all three mudflat based field stations is studied with the help of questionnaire, the base line data consisting of community status, life style, occupation etc. are developed. From the data, the living conditions and dependency on mangrove forests are analyzed. The relationship between utilization of resources and socio-economic conditions in each field station are compared. It is observed that the mangrove forests are utilized for fire/fuel wood, thatching of houses, temporary walls, boat manufacturing, traditional furniture, medicinal, fodder, tannin, fish nets, fish poisoning extracts etc. by the inhabitants.

Keywords: Mangroves, Mudflats, socio-economic, resource utilization

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I. Introduction

Mangroves comprise salt tolerant plant species that occur along inter-tidal zones of rivers and seas in the form of narrow strips or as extensive patches in estuarine habitats and river deltas of tropical and sub-tropical regions. Allen (1987), Luther and Greenburg (2009) identified that mangroves have been used by coastal inhabitants for centuries with the earliest reports. Mangroves provide a suite of provisioning ecosystem services, including: (i) fisheries production, Nagelkerken et al., (2000), Dorenbosch et al., (2004, 2005) (ii) aquaculture production Minh et al., (2001) (iii) pharmaceutical generation Abeysinghe, (2010) (iv) production of timber and fuelwood (the latter being important in the Caribbean and Pacific Lugo, (2002), Walters, (2005) and Walters et al., (2008). Human uses of mangrove resources have been categorized into traditional, commercial and destructive uses Field (1995). Uses of mangroves can be direct, involving the tangible benefits of mangrove forest products and mangrove-associated fisheries, or indirect, involving the intangible benefits of ecosystem services Saenger et al., (1983), Ewel et al., (1998), Hogarth (2007) and Walters et al., (2008). The former would entail the direct use of products from the ecosystem and the latter would rely on the use of the mangrove ecosystem as a whole Bandaranayake (1998).

II. Study Area

The present study is carried out to identify Mangroves vegetation utilization and socio-Economic aspects of people in mudflats based villages are given below.

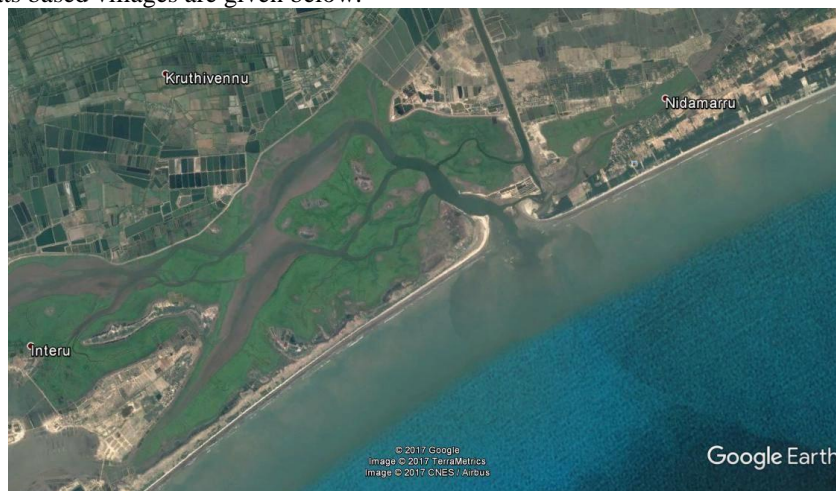


Figure-1: Satellite map showing the study areas

Interu:

Interu is a mid-sized village located at a distance of 36.5 km from Machilipatnam, it is under Kruthivenu mandal has 3 km coast line with high tide and low tide zone.

Kruthivenu:

Kruthivenu is a large village located at a distance of 44.7 km from Machilipatnam it is under Kruthivenu mandal has 5 km coast line with high tide and low tide zone.

Nidamaru:

Nidamaru is a large village located at a distance of 43 km from Machilipatnam, it is under Kruthivenu mandal has 2km coast line with high tide and low tide zone.

III. Materials And Methods

The socio-economic aspects Nabi et al (2012) and mangrove species utilization base line data are gathered from various selected houses in and around the field stations, by way of obtaining answers to the questionnaire, household form issued to each family. The data are analyzed from family to community and the socio-economic status and mangrove species utilization is estimated. The data on the aspects are generated with the help of physical observations, records of forest department and interviews with natives and NGOs. In addition, the parameters such as type of forestry operation in area and size and distance from the patch of natural vegetation or human habitation are also taken into consideration.

IV. Results

Mangrove vegetation in the study area consisting of 9 genera and 9 species of 5 families has been recorded as 6 trees, 1 shrubs and 2 herbs Prabhakar V.V et al (2017). The socio-economic situation among all field stations is studied with the help of questionnaire. From the responses to the questionnaire, the base line data consisting of community status, life style, occupation etc. are developed. From the data, the living conditions and dependency on mangrove forests are analyzed and the relationship between utilization of resources and socio-economic conditions in each field station are compared. It is observed that the mangrove forests are utilized for fire/fuel wood, thatching of houses, temporary walls, boat manufacturing, traditional furniture, medicinal, fodder, tannin, fish nets, fish poisoning extracts etc. by the inhabitants.

Socio- Economic status of the people in the study areas:

Socio-economic aspects of Interu:

In Interu village out of total population, 692 were engaged in work activities. 71.97 % of workers describe their work as Main Work (Employment or Earning more than 6 Months) while 28.03 % were involved in Marginal activity providing livelihood for less than 6 months. Of 692 workers engaged in Main Work, 12 were cultivators (owner or co-owner) while 120 were Agricultural labourers.

Most of the families have more than 4 members. Male to female sex ratio is 1:1. About 60.43% of the population is literate. Male literacy stands at 66.67 % while female literacy rate was 54.31 %. The annual income of most of the people is below ₹60000.

The plant species are used for traditional purpose and as subsistence for livelihood. The species *Avicennia marina*, *Bruguiera gymnorrhiza*, *Bruguiera cylindrica*, *Rhizophora mucronata*, *Acanthus ilicifolius*, *Ceriops decandra* are used for firewood, fodder, timber, tannin and medical purposes.

Socio-economic aspects of Kruthivenu:

In Kruthivenu village out of total population, 3847 were engaged in work activities. 50.82 % of workers describe their work as Main Work (Employment or Earning more than 6 Months) while 49.18 % were involved in Marginal activity providing livelihood for less than 6 months. Of 3847 workers engaged in Main Work, 277 were cultivators (owner or co-owner) while 1158 were Agricultural labourers.

Most of the families have more than 4 members. Male to female sex ratio is 1:1. About 65.66% of the population is literate. Male literacy stands at 68.28 % while female literacy rate was 63.07 %. The annual income of most of the people is below ₹60000.

The plant species are used for traditional purpose and as subsistence for livelihood. The species *Avicennia marina*, *Bruguiera gymnorrhiza*, *Bruguiera cylindrica*, *Rhizophora mucronata*, *Acanthus ilicifolius*, *Ceriops decandra* are used for firewood, fodder, timber, tannin and medical purposes.

Socio-economic aspects of Nidamaru

In Nidamaru village out of total population, 3735 were engaged in work activities. 65.62 % of workers describe their work as Main Work (Employment or Earning more than 6 Months) while 34.38 % were involved

in Marginal activity providing livelihood for less than 6 months. Of 3735 workers engaged in Main Work, 86 were cultivators (owner or co-owner) while 1325 were Agricultural labourer

Most of the families have more than 4 members. Male to female sex ratio is 1:1. About 58.37% of the population is literate Male literacy stands at 62.20 % while female literacy rate was 54.62 % . The annual income of most of the people is below ₹ 60000.

The plant species are used for traditional purpose and as subsistence for livelihood. The species *Avicennia marina*, *Bruguiera gymnorrhiza*, *Bruguiera cylindrica*, *Rhizophora mucronata*, *Acanthus ilicifolius*, *Ceriops decandra* are used for firewood, fodder, timber, tannin and medicinal purposes.

Table –2: Socio-economical status in the Study area

Detail Data		Interu	Kruthivenu	Nidamaru
House Hold - Families		180	2150	528
Total Population		692	7585	3735
Sex Ratio	Male	349	3763	1468
	Female	311	3822	2267
Family Size	4	135	1098	278
	>4	45	1052	300
Major Occupation	Agriculture	30	1158	1325
	Fishing	528	277	100
Literate Population		60.43%	65.66%	54.62%
Family Annual Income	<60000	120	50	508
	60000-100000	50	70	10
	>100000	20	30	10

LAND RESOURCE UTILIZATION

The land resource utilization in mudflats (Figure-2 a,b,c) is used for aquaculture and agriculture (mainly for paddy growing only very less amount of aquaculture ponds are reconverted into agricultural land in the recent years.

Cropping pattern:

The major agricultural crop that is cultivated in coastal villages near mangrove areas is paddy. Irrigation is mainly done by means of canals, channels, drains of Krishna river and upputeru. The forest department has raised casuarina plantation under its “Shelter-belt Programme” .The plantations are being raised by Vana Samrakshana Samiti (VSS), a village level society formed under Joint Forest Management programme of the Andhra Pradesh Forest Department in the non-sanctuary area.

Aquaculture:

Coastal aquaculture has been practiced for several hundred years both in revenue lands and forest areas; it has been part of the traditional livelihood for people living in mangrove areas. “Trapping and holding “operations, wild shrimp and other aquatic species, were carried into the pond by tidal flow, and were then harvested after a suitable interval of residence by the fishermen. In some places, paddy fields have been converted to prawn, crab farms; in other areas the same farms have been reconverted into paddy fields.

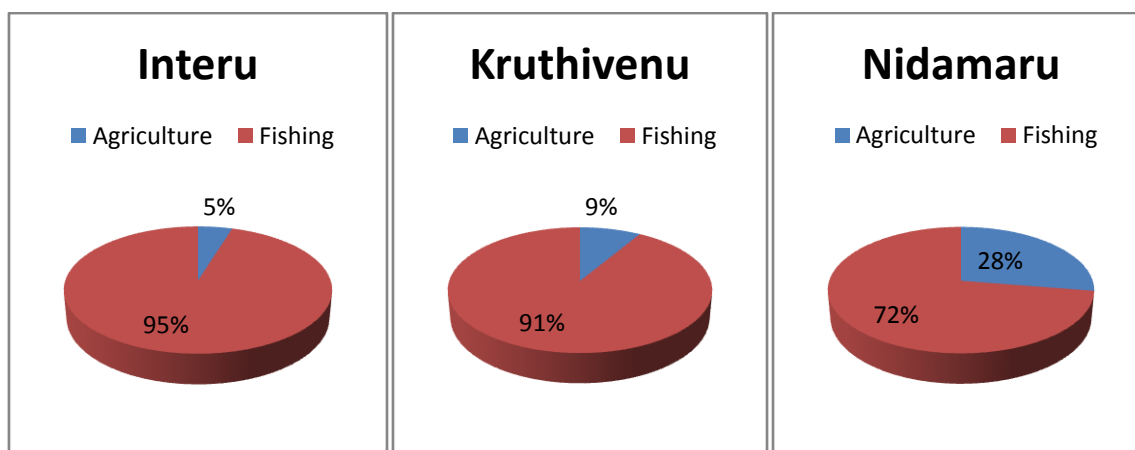


Figure-2: Land resource utilization in study area

V. Discussion

In study area over one-third of the households use wood from the mangroves for cooking Allen et al(2001) and Naylor et al(2002).The two species extracted primarily for fuel wood and also used as fences are *Rhizophora apiculata* and *Bruguiera gymnorhiza*.

The bark of *Ceriops decandra* is used for making dye for tanning fishing nets in Nidamaru .The bark of *Ceriops decandra* yields a brown coloured dye, which the fishermen use to preserve cotton fishing nets Raju et al., (2008) and also the ribs and keels of larger vessels such as the traditional boats like dhows are built from *Sonneratia alba*, *Heritiera littoralis* or *Avicennia marina* in Kenya Dahdouh-Guebas et al., (2000).

Excoecaria agallocha are used to catch fish, while branches and twigs with intact leaves are used mainly to catch shrimp in Kruthivenu regions Kapetsky (1981) As brush park fisheries require intensive labour, the introduction of brush parks as a fishing method creates employment and also used for pulp and paper Alam (2006).which is found in the study area which is used for paper making.

Cattle were fed with foliage of *Avicennia marina* (leaves, twigs and sometimes propagules) in both the regions and they been used for increasing milk production. It is evident that *Avicennia* foliage can be served both as feed and salt nutrient supplement for dairy cattle Maxwell & Lai (2012). The dependency of people and utilization of resources in this region were observed in a traditional and subsistence pattern.

VI. Conclusion

Socio-economic condition of the people in the study areas are poor, unemployment, seasonal agriculture and income generated is not sufficient to survive and to provide needs to family .this situation made them to shift to the income generating activity such as prawn seed collection, aquaculture, which are introduced in the recent past, have become popular, even though these are ecologically unsound. Recent development activities such as construction of bridge, roads and the proposal of major port and Satellite launching station threaten the existence of mangrove vegetation in this region.

Developmental activities will have a serious impact on the mangroves in study area. It is now increasingly recognized as neither politically feasible nor ethically justifiable to deny the poor from the use of natural resources without providing them alternative means of livelihood. In this context, ecological studies and the socio economic evaluation study in the area are needed for conservation, restoration and management practices.

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Vigorous attempts to Boost and buoying up MSMEs in India

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Abstract: In India, after agriculture, small business is the second largest employer of human resources. MSMEs constitute more than 80 percent of the total number of industrial enterprises and support industrial development, 40 per cent of industrial output, 80 per cent of employment in the industrial sector, 45 per cent of value added by the manufacturing sector and 40 per cent of total exports. In this paper an attempt is made to explain various schemes implemented by Ministry of Micro, Small and Medium Enterprises, Government of India for the promotion of MSMEs in India including general schemes, schemes for Khadi and Village Industries Sector, schemes for Coir Sector and schemes implemented by MSME Development Commissioner.

Key words: MSMEs, khadi industries, Village industries, coir board, promotional schemes

I. Introduction

MSME sector is one of the most crucial sectors of Indian economy as far as the number of employments generated. As more than 65 Percent of Indian population lives in rural and semi-rural areas, small business became a major source of income for many residing in these areas. After agriculture, small business in India is the second largest employer of human resources. In India, MSMEs constitute more than 80 percent of the total number of industrial enterprises and support industrial development, 40 per cent of industrial output, 80 per cent of employment in the industrial sector, 45 per cent of value added by the manufacturing sector and 40 per cent of total exports. Their contribution to the Indian GDP is 8% and the sector has registered growth rate of 10.8%. Micro, small and medium enterprises as per MSMED Act, 2006 are defined based on their investment in plant and machinery for manufacturing enterprise and on equipment for enterprises providing or rendering services.

Type of enterprise	Manufacturing enterprises (Investment limit in plant and machinery)	Service enterprises (Investment limit in Equipment)
Micro enterprise	Rs. 2.5 million / Rs. 25 lakh	Rs. 1 million / Rs. 10 lakh
Small enterprise	Rs.50 million / Rs. 5 crore	Rs. 20 million / Rs 2 crore
Medium enterprise	Rs 100 million / Rs 10 crore	Rs. 50 million / Rs 5 crore

II. Review Of Literature

Venugopal (1993)¹ found that the government organizations' performances, which were set up for promoting village and cottage industries, are below the level of expectations. Cecile Carpenter and Jean Marc Suret (2005)² reviewed the taxation policy introduced by the government for the progress of the MSME sector. They suggested that there is an urgent need to introduce more result-oriented measures; if not tax incentive initiatives will remain ineffective. Jogendra Kumar Nayak et al (2006)³ studied the perceptions of managers regarding the reasons for outsourcing and the impact of outsourcing in small and medium enterprises. Prof. B.Appa Rao (2007)⁴ conducted a survey on policy framework of SMEs sector. He found that the incentives that are offered by the selected countries towards promotion of SMEs are mainly in the form of tax reliefs, subsidies, soft credit facilities, preferential treatment in government policies etc. T. Gopi (2009)⁵ studied the promotional policy measures for the development of small entrepreneurs from time to time. Anthony K. Ahiawodzi and Thomas C. Adade (2012)⁶ had developed an econometric model to examine the impact of various factors on the development of the MSME sector. They found that access to credit is the most dominant factor in case of firm's overall development. Bhoomika Garg (2014)⁷ has studied the challenges that the Indian MSME sector is facing along with the government policy considerations. Ashu Katyal and Betsy Xaviour (2015)⁸ expressed the view that MSME sector has greater role for the overall economic development in India. They also said that MSMEs have the capacity to absorb low skilled workers who are otherwise left unemployed. It is concluded that there was no study which dealt comprehensively with the schemes introduced in India for the development of MSMEs.

III. Objectives

The main objective is to present the schemes introduced and implemented to promote MSMEs in India. The specific objectives are the following.

1. To examine the general schemes introduced by ministry of Micro, Small and Medium Enterprises, Government of India for the promotion of MSMEs in India.
2. To list out the schemes being implemented for Khadi and Village Industries Sector.
3. To describe the schemes relating to coir sector.
4. To present the schemes being implemented by MSME Development Commissioner

IV. Methodology

The present study is a descriptive study. An attempt is made to review the existing literature on MSMEs in India. After extensive survey of the literature it is found that there was no specific study which dealt with schemes for boosting and buoying up MSMEs in India. In this paper an attempt is made to review various schemes introduced to promote MSMEs in India. The schemes are broadly covered under the headings of A) General schemes, B) Schemes for Khadi and Village Industries Sector, C) Schemes for Coir Sector and D) Schemes implemented by MSME Development Commissioner.

V. Schemes Introduced To Boost And Buoying Up Msmes In India

A. General schemes

Marketing Assistance Scheme

This scheme is being implemented by the ministry of Micro, Small and Medium Enterprises through National Small Industries Corporation Limited (NSIC). This scheme is introduced with the objectives of enhancing the marketing competitiveness of MSMEs, providing them a platform for interaction with the individual or institutional buyers, updating them with prevalent market scenario and to provide them a form for redressing their problems.

International Cooperation (IC) Scheme

Under this scheme assistance is given to Indian MSMEs to infuse, to upgrade technology, to modernize and promote their exports. Activities in the scheme include 1. deputation of business delegations to other countries to explore new areas of technology infusion or up gradation, facilitating foreign collaborations and improving markets for MSMEs 2. Providing support to MSMEs in participating in international exhibitions and trade fairs 3. providing assistance for organizing seminars and conferences on themes of MSMEs.

Performance and Credit Rating Scheme

This scheme is being implemented by NSIC. Through this scheme financial assistance is provided to MSMEs for getting credit rating by the agencies like CRISIL, ICRA and CARE.

Assistance to Training Institutions Scheme

This scheme provides financial assistance for strengthening the infrastructure of the existing Entrepreneurship Development Institutes, for establishing of new Entrepreneurship Development institutions and for supporting entrepreneurship and skill development activities. The assistance is provided in the form of capital grant.

Survey, Studies and Policy Research Scheme

This scheme provides financial support for collecting regular and periodical data on various aspects of MSMEs in India. The scheme also provides financial support to study and analyze the constraints and challenges as well as opportunities faced by MSMEs. This scheme also helps to use the surveys and studies for policy research.

A Scheme for Promoting Innovation and Rural Entrepreneurship (ASPIRE)

This scheme was launched by the ministry of Micro, Small and Medium Enterprises on 18.3.2015. The main objective of the scheme is to set up a network of technology centers and incubation centers to accelerate entrepreneurship and also to promote start-ups for innovation and entrepreneurship in agro-industry. The important components are to set up Livelihood Business Incubators (LBI), Technology Business Incubators (TBI) and to create a framework for start-up promotion through Small Industries Development Bank of India (SIDBI).

B. Schemes for Khadi and Village Industries Sector

Prime Minister's Employment Generation Programme (PMEGP)

This is a credit linked subsidy scheme. This scheme is implemented by the of the ministry of Micro, Small and Medium Enterprises through KVIC, DICs and State KVI Boards with KVIC by setting up new self-employment

ventures or projects or micro enterprises to generate employment opportunities in rural and urban areas of the country. The idea is to bring together widely dispersed traditional artisans or rural and urban unemployed youth and give them self employment opportunities.

Scheme of fund for Regeneration of Traditional Industries (SFURTI)

This scheme was introduced with the objective of making the traditional industries more productive and competitive and facilitating their sustainable development. This objective is achieved by creating a fund for regeneration of traditional industries and by organizing the traditional industries and artisans into clusters.

Market Promotion and Development Assistance (MPDA)

The MDA scheme of KVIC was modified as Market Promotion Development Assistance scheme (MPDA). This scheme is formulated by merging different schemes and sub-schemes including Market Development Assistance, Publicity, Marketing and Market promotion and adds a new component of Infrastructure including Marketing complexes or Khadi Plaza.

C. Schemes for Coir Sector

Coir Vikas Yojana

Under this scheme coir board adopted strategic and aggressive product specific and market specific promotional programmes for popularizing coir and coir products in markets abroad. Through this scheme assistance is provided for the entrepreneurs in coir industry to participate in international fairs, product promotion programmes and seminars.

Coir Udyami Yojana

Under this scheme, Government provides assistance to replace the outdated rats and looms. Assistance is also provided to spinners and tiny household units for constructing work sheds to increase production and earnings of workers. The main goal of the scheme is to provide assistance for rejuvenating, modernizing and technologically upgrading spinners and tiny household sector.

Coir S & T Yojana

This scheme is also known as 'Science and Technology Scheme'. This scheme is being implemented by the coir board with the help of Central Coir Research Institute, Kalavoor and the Central Institute of Coir Technology, Bangalore. With the help these research institutions; the Board is developing many new eco-friendly technologies, processes, diversified products, equipments and machinery for increased productivity and efficiency of the coir products.

D) Schemes implemented by MSME Development Commissioner

Credit Guarantee Scheme (CGTMSE)

This scheme was introduced to strengthen credit delivery system and facilitate flow of credit to the MSE sector. Through this scheme, loans up to Rs. 100 lakh without collateral and third party guarantees are being provided to SMEs. Under this scheme, the Government reassures the lender that, in the event of a MSE unit fails to discharge its liabilities to the lender; the CGTMSE would make good the loss incurred by the lender.

Credit Linked Capital Subsidy Scheme (CLCSS)

This scheme is being implemented to facilitate technological up gradation by new and existing Micro and Small Enterprises (MSEs) engaged in manufacturing. Through this scheme, 15percent upfront capital subsidy to a maximum limit of Rs.15.00 lakhs is given to MSEs for induction of well-established and improved technologies. This scheme covers 51 sub-sectors or products with approved machinery and technologies.

Micro and Small Enterprises Cluster Development Programme (MSE-CDP)

This scheme was introduced by the ministry of Micro, Small and Medium Enterprises for enhancing the productivity and competitiveness as well as capacity building of Micro and Small Enterprises (MSEs) and their collectives in the country. As per the scheme the cluster is defined as a group of enterprises located within an identifiable and as far as practicable, contiguous area and producing same or similar products or services. The objectives of the scheme include providing support for sustainability and growth of MSEs by addressing common issues, building capacity of MSEs for common supportive action through formation of self help groups, consortia, up gradation of associations, etc. and to common facility centers.

Lean Manufacturing scheme

This scheme was introduced to enhance the manufacturing competitiveness of MSMEs through the application of various Lean Manufacturing (LM) techniques like 5S system, visual control, standard operating procedures (SOPs), Just in Time (JIT), KANBAN System, Cellular Layout, Value Stream Mapping, Single Minutes Exchange of Dies (SMED), and Total Productive Maintenance.

Financial Design Clinic Scheme

This scheme was introduced to create a sustainable design eco system for the MSME sector through continuous learning and skill development.

Information and Communication Technology scheme

This scheme was introduced to promote an eco system of cost effective and all inclusive ICT applications for MSMEs through Cloud Computing. In this scheme, to encourage MSMEs to use Cloud Computing for ICT applications, the Government provides subsidy for user charges for a period of 3 years. The idea is that the benefits accrued through implementing ICT for subsidy period in their enterprises will motivate MSMEs to continue to use the ICT application with their own expenses after this period.

Intellectual Property Rights scheme

This scheme was introduced to enhance awareness of MSMEs about Intellectual Property Rights (IPRs), to take measures for the protecting their ideas and business strategies, to assist SMEs in technology up-gradation and enhancing competitiveness and for effective Utilization of IPR tools by MSMEs and to sensitize Entrepreneurs on IPR related matters by providing financial assistance for taking up the identified initiatives.

Incubation scheme

Under this scheme the Government is providing opportunity to the innovators in developing and nurturing their new innovative ideas for the production of new innovative products which can be sent in to the market for commercialization. This Ministry has been implementing this scheme since 2008. Financial support is given through the business incubator (BIs). The BIs may be engineering colleges approved by AICTE, central or state universities recognized by UGC and other recognized institutions.

Bar Code Scheme

This scheme was introduced to enhance marketing competitiveness of Micro and Small Enterprises (MSEs) by popularizing the adoption of bar codes, motivating and encouraging MSEs for use of bar codes through conducting seminars. Some financial assistance is also provided in the form of reimbursing 75 percent of one time registration fee.

Marketing Development Assistance (MDA) Scheme

This scheme was introduced with the objectives of encouraging small and micro enterprises in tapping and developing overseas markets, increasing participation of representatives of small and micro manufacturing enterprises under MSME India stall at international trade fairs and exhibitions and to enhance exports from the small and micro manufacturing enterprises.

ZED Maturity Model: Quality Management Standards (QMS) and Quality Technology Tools (QTT) scheme

The main activities of the scheme include conducting one day awareness campaign, two days workshop at Metros, one National level workshop at Delhi, implementation of Quality Management Standards (QMS) and Quality Technology Tools (QTT) in selected MSEs Cluster through various expert agencies or organizations.

Trade Related Entrepreneurship Assistance and Development (TREAD) for Women

The main objective of the scheme is to empower women through trade related training, information and counseling extension activities related to MSME trades, products, services and so on. As per this scheme financial loans are provided through NGO's who are also provided Government of India grant for capacity building. The Assistance is provided for self-employment ventures by women for pursuing different nonfarm activities.

Public Procurement Policy Vendor Development Programme

This scheme was introduced to create and enhance marketing linkages between Indian SMEs and Public Sector Units like BEL, BHEL, TELCO, BSNL and IOC for their mutual benefit.

Marketing Assistance and Technology Up-gradation (MATU) scheme

This scheme is useful for MSMEs for enhancing competitiveness in national and international markets by adopting better packaging technologies, modern marketing strategies and encouraging them to acquire ISO certification and Bar Codes for making their products more acceptable to the consumers.

Technology Centre Systems Programme

The main objective of the scheme is making MSMEs globally competitive through access to advanced manufacturing technologies.

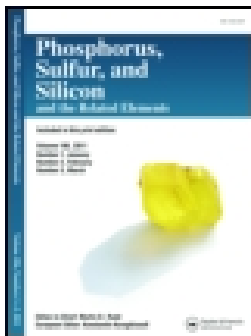
Technology and Quality up gradation Support to MSMEs

This scheme was introduced to encourage the MSMEs to acquire product certification or licenses from National and International bodies and adopt other technologies mandated as per the global standards.

VI. Conclusion

Various policies and schemes are being implemented by Ministry of Micro, Small and Medium Enterprises, Government of India for promoting MSMEs in India. Schemes are being modified and up dated from time to time. Most of the schemes provide financial support for MSMEs to market their products, to update their technologies and to become more competitive. No doubt, Indian MSMEs are getting boosted up and Buoying up through these vigorous attempts. Further research is required for examining the impact of these schemes.

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DESIGN, GREEN SYNTHESIS, ANTI-MICROBIAL AND ANTI-OXIDANT ACTIVITIES OF NOVEL α -AMINOPHOSPHONATES VIA KABACHNIK-FIELDS REACTION

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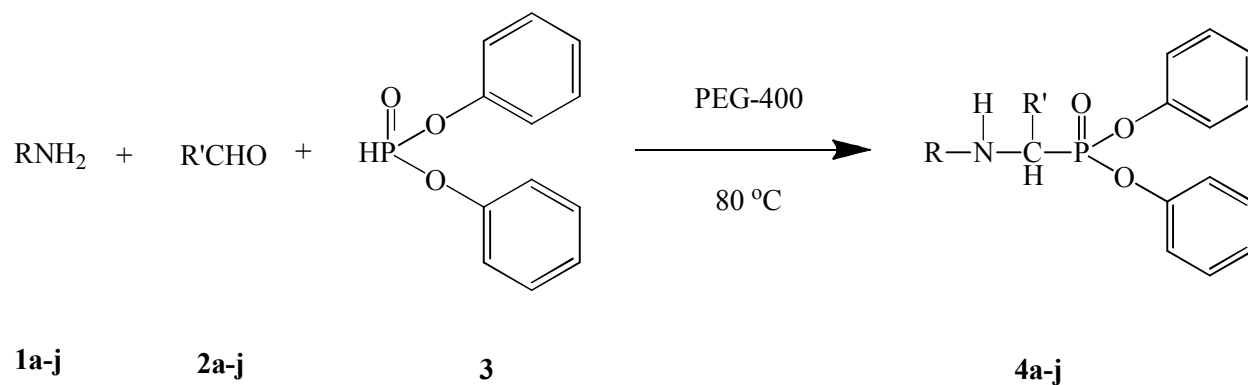
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Abstract

An efficient and environmentally friendly protocol has been developed for the synthesis of novel α -Aminophosphonates in good to excellent yields (76-92 %) by a one-pot, three-component reaction of an amine, an aldehyde, and diphenyl phosphite using polyethylene glycol (PEG-400) as a green solvent at 80 °C via Kabachnik–Fields reaction. Their chemical structures were elucidated by IR, ¹H, ¹³C and ³¹P NMR spectroscopy, mass spectrometry and elemental analysis. The titled compounds displayed moderate to high anti-microbial and anti-oxidant activities.

**Keywords**

α -Aminophosphonates; Kabachnik-Fields reaction; green synthesis; anti-microbial activity; anti-oxidant activity

INTRODUCTION

The treatment of infectious diseases still remains an important and challenging problem because of an emergence of an increasing number of multi-drug resistant microbial pathogens. Indeed, there is a real need for the discovery of novel compounds endowed with anti-microbial activity. Researchers worldwide are focussing to develop better remedies for infectious diseases.

Organophosphorus compounds are biologically active molecules and show a wide range of applications in industrial, agricultural and medicinal chemistry owing to their unique physicochemical properties. Several commercially available phosphorus containing diols represent flame retardants for a variety of application in different polymers, such as epoxy resins, polyurethane foams and polyester fibers. Their utility as reagents and potential synthons in organic synthesis is gaining increased attention.¹ α -Aminophosphonates are the structural analogs of α -amino acids, and have received wide attention in bioorganic, medicinal, and agricultural chemistry. α -Aminophosphonates and their derivatives have significant applications in agriculture as plant regulators, herbicides,⁴ pesticides and in medicine as anti-cancer agents,⁵ enzyme inhibitors,⁶ peptide mimics,⁷ antibiotics,⁸ and pharmacological agents.⁹

A great range of synthetic methods have been established for the synthesis of α -Aminophosphonates. A one-pot, three-component reaction of aldehydes (or ketones), amines, and dialkyl, or diarylphosphites via Kabachnik-Fields reaction¹⁰ is one of the most attractive options for the formation of carbon-phosphorus bonds. In some reports, this reaction was carried out in straight-forward one-pot procedures without any catalysts.^{11, 12} In most cases, however, it was performed using catalysts such as BiCl_3 ,¹³ $\text{TaCl}_5\text{-SiO}_2$,¹⁴ InCl_3 ,¹⁵ lanthanide-triflate¹⁶ and SbCl_3 .¹⁷ Nevertheless, there remains a need to develop a more efficient method, particularly from

the view point of today's environmental concerns about environmental pollution. Environmentally benign methods for the synthesis of pharmaceutically and industrially important compounds are in extreme demand.¹⁸ The most important principles of green chemistry are atom economy, less usage or no wastage of solvents and usage of green solvents. The usage of an obviously benign and low-priced solvent like PEG could consequently yield noteworthy "green" chemistry benefits. Polyethylene glycol (PEG) has attracted great interest and has been explored as a novel, powerful, eco-friendly reaction medium for various organic transformations due to their excellent properties such as non-toxicity, inexpensive, readily recyclable, and thermally stable.

In this contribution and continuance of our attention in developing novel biologically important organophosphorus compounds¹⁹ and green synthetic procedures, we disclose an efficient and eco-friendly protocol for the synthesis of novel α -Aminophosphonates by using polyethylene glycol (PEG-400) as a recyclable reaction medium at 80 °C via Kabachnik-Fields reaction (Scheme 1). All the synthesized, novel α -Aminophosphonate compounds were further evaluated for their anti-microbial and anti-oxidant activities.

[Insert Scheme 1]

RESULTS AND DISCUSSION

In a typical experiment, a one-pot, three-component reaction of an amine (0.001 mol), aldehyde (0.001 mol) and diphenyl phosphite (0.001mol) were reacted in the presence of polyethylene glycol (PEG-400) at 80 °C for 2 h. The progress of the reaction was monitored by TLC and the products were purified by silica gel column chromatography to afford the pure α -

Aminophosphonates (Scheme 1). PEG-400 proved to be more efficient in increasing the yields, diminished reaction times, inexpensive, biodegradable non-hazardous solvent.

Keeping in view of the concerns about environmental pollution, a green and suitable solvent PEG has been used as an alternative reaction medium to perform organic synthesis due to its natural advantages over toxic solvents. In this synthesis, PEG-400 not only acts as the solvent but also speed up the imine formation and nucleophilic addition of phosphite to the imine by increasing its electrophilicity through hydrogen bonding by its hydroxyl group with the imine nitrogen.

The structures of the title compounds (**4a-j**) were confirmed by spectral and analytical data. The characteristic IR stretching absorptions were observed in the region 3421-3346 cm^{-1} (NH), 1249-1202 cm^{-1} (P=O) and 769-745 cm^{-1} (P-C_(aliphatic)) respectively.²⁰ In ^1H NMR, chemical shifts for aromatic protons of the titled compounds appeared as a complex multiplet in the region δ 6.34-8.44 ppm.²¹ The chemical shift of the proton of methyne (P-C-H) appeared as a doublet of doublets²¹ at δ 5.20-5.85 and 5.67-5.82 due to its coupling with phosphorus and the neighbouring N-H proton. The N-H proton exhibited a triplet²¹ at δ 4.30-5.44 indicating its coupling with neighbouring proton and phosphorus. The ^{13}C NMR chemical shifts for the titled compounds were observed in the expected region.²² ^{31}P NMR chemical shifts appeared as singlets in the region δ 18.4-27.2 for all the compounds.²³ The LC mass spectra of all the compounds agreed with the proposed structures.

Biological activity

Preliminary anti-bacterial activities of the titled compounds were evaluated by screening against gram positive bacteria and gram negative bacteria by the disc diffusion method. The results were compared with the standard drug Streptomycin. The results shown that the majority of the synthesized compounds showed varying degrees of inhibition against the tested microorganisms and are presented in the Supplemental Materials (Table S 1)

The titled compounds were tested for anti-fungal activity and the results were compared with the standard drug Bovastin (Table S 2 Supplemental Materials).

The preliminary anti-oxidant activities were tested at 50, 100, 200, 400 and 600 $\mu\text{g/mL}$ concentrations for the all the titled compounds (Table S 3, Supplemental Materials).

CONCLUSION

We have developed an efficient and eco-friendly synthesis of novel α -Aminophosphonates in good to excellent yields (76-92%) and these compounds are potentially valuable to be as bioactive molecules and pharmacological agents. In these reactions, PEG-400 acts as an efficient “green” promoter. Moreover, all the synthesized compounds displayed moderate to high anti-bacterial, anti-fungal, and anti-oxidant activities. The significant features of this protocol are environmental acceptability, avoiding hazardous solvents and toxic organic reagents, simple work-up procedure, relatively high yields, cleaner reaction profiles, mild experimental conditions, inexpensive, biodegradable non-toxic solvent, potentially useful biologically active compounds.

EXPERIMENTAL

All chemicals and reagents were from Sigma-Aldrich and were used without further purification. Solvents used for spectroscopic and physical studies were reagent and were further purified by the literature methods.²⁴ Melting points were determined in open capillaries on a Mel-Temp apparatus and are uncorrected. Thin-layer chromatography (TLC) was performed using Merck aluminium-backed plates (Kieselgel 60 F₂₅₄), and visualization was achieved by UV light. Crude products were purified by column chromatography on silica gel of 60-120 mesh. The infrared (IR) spectra were recorded as KBr pellets on a Perkin-Elmer FT-IR 1000 spectrophotometer. ¹H, ¹³C, and ³¹P NMR spectra were recorded as solutions in CDCl₃ on a Varian 400 MHz spectrometer operating at 400 MHz for ¹H, 100 MHz for ¹³C, and 300 MHz for ³¹P NMR. The ¹H and ¹³C chemical shifts were expressed in ppm using tetramethylsilane (TMS) as an internal standard and ³¹P NMR chemical shifts to 85% H₃PO₄. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants (*J*) in hertz (Hz). ESI mass spectra were recorded on an LCMS-2010A Shimadzu spectrometer and elemental analysis was performed on a Thermo Finnigan instrument. The Supplemental Materials contains sample ¹H, ¹³C and ³¹P NMR spectra of 4a, 4e and 4h (Figures S 1 – S 9)

General procedure for the synthesis of novel α -Aminophosphonates

To a mixture of 2-Aminothiazole (**1a**) (0.10 g, 0.001 mol), 2-pyridine aldehyde (**2a**) (0.10 g, 0.001 mol), diphenyl phosphite (**3**) (0.23 mL, 0.001 mol) and PEG-400 (15 mL) were successively added by one-pot, three-component method and then the mixture was stirred at 80 °C for 2 h according to Scheme 1. The progress of the reaction was monitored by thin-layer chromatography (TLC) (hexane: ethyl acetate, 7:3). After completion of the reaction, the crude

mixture was worked up in ice-cold water. The product that separated out was filtered and the filtrate was evaporated to remove water, leaving PEG behind. The same PEG was utilized to synthesize further α -Aminophosphonates. This crude product was further purified by column chromatography on silica gel (60-120 mesh) using hexane: ethyl acetate (7:3) as a mobile phase to afford the analytically pure compound, diphenyl [pyridine-2-yl (thiazol-2-ylamino) methyl] phosphonate (**1a**).

All other compounds were synthesized by adopting the same experimental procedure (Scheme 1).

Diphenyl [pyridine-2-yl (thiazol-2-ylamino) methyl] phosphonate (**4a**)

Brown solid, yield 84%, m.p: 183-185 °C. IR: 3421 (NH), 1205 (P=O), 760 (P-C_{aliphatic}); ¹H NMR: 4.72 (t, 1H, *J*= 11.3 Hz, NH), 5.61 (dd, 1H, *J*=10.2 Hz, *J*=17.3 Hz, P-C-H), 6.69 (d, 1H, *J*= 18.2 Hz, Ar-SCH), 7.14 (d, 1H, *J*= 21.0 Hz, Ar-NCH), 7.18-8.35 (m, 14H, ArH); ¹³C NMR: 56.3 (C₇), 109.2 (C₁), 117.5 (C₁₁,C₁₅,C₂₅,C₂₉), 120.7 (C₁₉), 121.3 (C₁₃,C₂₇), 124.4 (C₁₇), 130.1 (C₁₂,C₁₄,C₂₆, C₂₈), 135.5 (C₁₈), 139.1 (C₂), 147.2 (C₂₀), 154.3 (C₁₀, C₂₄), 158.1 (C₁₀, C₂₄), 167.3 (C₃); ³¹P NMR: 21.3, LC-MS (*m/z*, %): 424 (100) [M+H]⁺. Calcd. for C₂₁H₁₈N₃O₃PS: C, 59.57; H, 4.28; N, 9.92. Found: C, 59.46; H, 4.31; N, 9.85.

Diphenyl [pyridine-3-yl (thiazol-2-ylamino) methyl] phosphonate (**4b**)

Brown solid, yield 87%, m.p: 201-203 °C. IR: 3351 (NH), 1220 (P=O), 748 (P-C_{aliphatic}); ¹H NMR: ¹H NMR: 4.45 (t, 1H, *J*= 12.6 Hz, NH), 5.34 (dd, 1H, *J*=20.5 Hz, *J*=21.4 Hz, P-C-H), 6.74 (d, 1H, *J*= 10.5 Hz, Ar-SCH), 7.12 (d, 1H, *J*= 14.0 Hz, Ar-NCH), 7.23-8.56 (m, 14H, ArH); ¹³C NMR: 57.6 (C₂₂), 110.2 (C₂₈), 119.1 (C₆,C₁₀,C₁₄, C₁₈), 121.1 (C₈, C₁₆), 123.2 (C₃), 129.2

(C₇,C₉,C₁₅,C₁₇), 131.6 (C₅), 134.2 (C₄), 138.1(C₂₇), 146.5 (C₂), 148.1 (C₂₉), 152.4 (C₁₁,C₁₉), 168.2 (C₂₅); ³¹P NMR: 24.1, LC-MS (*m/z*, %): 423 (100) [M]⁺. Calcd. for C₂₁H₁₈N₃O₃PS: C, 59.57; H, 4.28; N, 9.92. Found: C, 59.63; H, 4.22; N, 9.81.

Diphenyl [{1*H*-indol-3-yl} (thiazol-2-ylamino) methyl] phosphonate (4c)

Yellow solid, yield 91%, m .p: 176-178 °C. IR: 3357 (NH), 1213 (P=O), 745 (P-C_{aliphatic}); ¹H NMR: 4.83 (t, 1H, *J*= 22.5 Hz, NH), 5.74 (dd, 1H, *J*=16.3 Hz, *J*=11.4 Hz, P-C-H), 6.51 (d, 1H, *J*= 10.4 Hz, Ar-SCH), 7.17 (d, 1H, *J*= 18.5 Hz, Ar-NCH), 7.22-7.61 (m, 16H, ArH); ¹³C NMR: 61.7 (C₂₃), 109.2 (C₂₅),111.2 (C₁), 112.5 (C₂₂), 113.7 (C₂₂), 117.5 (C₉,C₁₃,C₁₇,C₂₁), 118.0 (C₃₀), 119.1 (C₃₀), 122.3 (C₃₂), 121.0 (C₃₁), 122.2 (C₅), 123.6 (C₁₂,C₁₉), 127.4 (C₁₀, C₁₂,C₁₈,C₂₀), 131.6 (C₂), 136.4 (C₃),138.7 (C₂₆),151.3 (C₈,C₁₆),166.2 (C₂₈); ³¹P NMR: 24.2, LC-MS (*m/z*, %): 460 (100) [M-H]⁺. Calcd. for C₂₄H₂₀N₃O₃PS: C, 62.46; H, 4.37; N, 9.11. Found: C, 62.38; H, 4.46; N, 9.18.

Diphenyl [{3-nitrophenyl} (thiazol-2-ylamino) methyl] phosphonate (4d)

Yellow solid, yield 90%, m.p: 184-186 °C. IR: 3414 (NH), 1225 (P=O), 751 (P-C_{aliphatic}); ¹H NMR: 4.92 (t, 1H, *J*= 17.2 Hz, NH), 5.73 (dd, 1H, *J*=8.5 Hz, *J*=15.4 Hz, P-C-H), 6.61 (d, 1H, *J*= 21.2 Hz, Ar-SCH), 7.23 (d, 1H, *J*= 13.3 Hz, Ar-NCH), 7.31-8.15 (m, 14H, ArH); ¹³C NMR: 58.4 (C₇), 111.4 (C₅), 117.1 (C₁₁,C₁₅,C₂₀,C₂₄), 121.2 (C₁₃,C₂₂), 122.5 (C₂₇), 123.7 (C₂₇), 129.1 (C₂₆), 129.8 (C₁₂,C₁₄,C₂₁,C₂₃), 134.2 (C₂₅), 137.4 (C₄), 146.5 (C₁₆), 148.1 (C₂₈), 150.4 (C₁₀,C₁₉), 162.2 (C₂); ³¹P NMR: 21.4, LC-MS (*m/z*, %): 468 (100) [M+H]⁺. Calcd. for C₂₂H₁₈N₃O₅PS: C, 56.53; H, 3.88; N, 8.99. Found: C, 56.47; H, 3.92; N, 8.82.

Diphenyl [{naphthalene-1-ylamino}(pyridin-3-yl) methyl] phosphonate (4e)

Brown solid, yield 86%, m.p: 141-143 °C. IR: 3409 (NH), 1230 (P=O), 757 (P-C_{aliphatic}); ¹H NMR: 4.94 (t, 1H, *J*= 18.3 Hz, NH), 5.76 (dd, 1H, *J*=17.2 Hz, *J*=10.3 Hz, P-C-H), 7.24-8.57 (m, 21H, ArH); ¹³C NMR: 59.2 (C₅), 104.5 (C₃₂), 118.7 (C₃₀), 120.6 (C₃₄), 121.5 (C₁₁, C₂₀), 123.3 (C₂₄), 124.4 (C₃₃), 125.2 (C₁), 126.5 (C₃₁), 128.7 (C₂), 128.5 (C₁₀,C₁₂,C₁₉,C₂₁), 132.2 (C₁₄), 133.6 (C₂₉), 134.0 (C₂₃), 149.1 (C₃), 149.9 (C₂₅), 158.3 (C₂₇), 162.4 (C₈, C₁₇); ³¹P NMR: 23.1, LC-MS (*m/z*, %): 467 (100) [M+H]⁺. Calcd. for C₂₈H₂₃N₂O₃P: C, 72.09; H, 4.97; N, 6.01. Found: C, 71.96; H, 4.89; N, 6.09.

Diphenyl [{1*H*-indol-3-yl} (naphthalene-1-ylamino) methyl] phosphonate (4f)

Brown solid, yield 93%, m.p: 157-159 °C. IR: 3362 (NH), 1240 (P=O), 752 (P-C_{aliphatic}); ¹H NMR: 4.86 (t, 1H, *J*= 22.1 Hz, NH), 5.82 (dd, 1H, *J*=14.1 Hz, *J*=21.2 Hz, P-C-H), 7.16-8.13 (m, 22H, ArH), 10.21 (s, 1H, Ar-NH); ¹³C NMR: 58.5 (C₇), 107.2 (C₃₂), 111.7 (C₂₈), 112.5 (C₄), 115.1 (C₁₁, C₁₅,C₁₉,C₂₃), 118.3 (C₃₅), 119.1 (C₂₉), 120.5 (C₃₁), 121.7 (C₃), 122.2 (C₂₄), 123.6 (C₃₇), 124.3 (C₂), 125.0 (C₁), 126.7 (C₃₄), 128.1 (C₃₃), 129.3 (C₁₃,C₁₅,C₂₀,C₂₂), 130.3 (C₂₇), 134.2 (C₃₆), 136.2 (C₂₆), 143.2 (C₅), 150.1(C₁₀,C₁₈); ³¹P NMR: 23.2, LC-MS (*m/z*, %): 504 (100) [M]⁺. Calcd. for C₃₁H₂₅N₂O₃P: C, 73.80; H, 4.99; N, 5.55. Found: C, 73.68; H, 5.04; N, 5.62.

Diphenyl [{naphthalene-1-ylamino} (3-nitrophenyl) methyl] phosphonate (4g)

Yellow solid, yield 87%, m.p: 170-172 °C. IR: 3349 (NH), 1232 (P=O), 760 (P-C_{aliphatic}); ¹H NMR: 4.56 (t, 1H, *J*= 13.5 Hz, NH), 5.72 (dd, 1H, *J*=10.8 Hz, *J*=24.5 Hz, P-C-H), 7.21-8.12 (m, 21H, ArH); ¹³C NMR: 59.1 (C₁₀), 109.4 (C₅), 116.5 (C₁₆,C₂₀,C₂₅,C₂₉), 118.3 (C₃), 120.3 (C₆), 121.0 (C₁₈,C₂₇), 122.1 (C₃₄), 126.5 (C₄), 128.4 (C₉), 129.3 (C₃₁), 129.9 (C₁₇,C₁₉, C₂₆,C₂₈), 132.1

(C₃₀), 135.5 (C₂), 142.0 (C₁₂), 145.2 (C₂₁), 148.3 (C₃₃), 154.6 (C₁₅,C₂₄); ³¹P NMR: 25.1, LC-MS (*m/z*, %): 510 (100) [M]⁺. Calcd. for C₂₉H₂₃N₂O₅P: C, 68.23; H, 4.54; N, 5.49. Found: C, 68.34; H, 4.38; N, 5.64.

Diphenyl [{1, 1'-biphenyl-4-ylamino} (pyridine-3-yl) methyl] phosphonate (4h)

Brown solid, yield 91%, m.p.: 183-185 °C. IR: 3377 (NH), 1234 (P=O), 740 (P-C_{aliphatic}); ¹H NMR: 4.94 (t, 1H, *J*= 23.0 Hz, NH), 5.81 (dd, 1H, *J*=14.3 Hz, *J*=11.5 Hz, P-C-H), 7.17-8.53 (m, 23H, ArH); ¹³C NMR: 58.1 (C₃), 110.1 (C₂₉,C₃₁), 115.8 (C₅,C₉,C₁₆,C₂₀), 121.2 (C₇,C₁₈), 121.7 (C₂₆), 127.5 (C₃₂,C₃₄,C₃₆), 128.0 (C₂₇,C₂₈), 129.1 (C₃₃,C₃₅), 129.8 (C₆,C₈,C₁₇,C₁₉), 132.6 (C₁₀), 134.4 (C₂₁), 138.3 (C₃₀), 144.1 (C₁), 145.1 (C₂₃), 155.5 (C₂₅), 160.0 (C₁₄,C₁₅); ³¹P NMR: 22.1, LC-MS (*m/z*, %): 493 (100) [M+H]⁺. Calcd. for C₃₀H₂₅N₂O₃P: C, 73.16; H, 5.12; N, 5.69. Found: C, 73.28; H, 5.24; N, 5.71.

Diphenyl [{1, 1'-biphenyl-4-ylamino} (1*H*-indol-3-yl) methyl] phosphonate (4i)

Brown solid, yield 88%, m.p.: 154-156 °C. IR: 3354 (NH), 1210 (P=O), 754 (P-C_{aliphatic}); ¹H NMR: 4.68 (t, 1H, *J*=19.1 Hz, NH), 5.72 (dd, 1H, *J*=21.8 Hz, *J*=22.2 Hz, P-C-H), 7.32-7.62 (m, 24H, ArH), 7.20 (s, 1H, Ar-NH); ¹³C NMR: 58.4 (C₄), 111.4 (C₂₅), 112.7 (C₁), 113.3 (C₂₉,C₃₃), 115.7 (C₈,C₁₂,C₁₆,C₂₀), 119.5 (C₂₆), 120.2 (C₂₈), 121.4 (C₁₀,C₁₈), 121.7 (C₂₇), 123.1 (C₂₁), 125.0 (C₃₁), 127.2 (C₃₅,C₃₇,C₃₉), 128.3 (C₃₀,C₃₂), 129.4 (C₃₆,C₃₈), 129.9 (C₉,C₁₁,C₁₇,C₁₉), 131.6 (C₂₄), 136.4 (C₃₄), 136.5 (C₂₃), 157.3 (C₇,C₁₅) 141.4 (C₅), 156.6 (C₇,C₁₅); ³¹P NMR: 21.0, LC-MS (*m/z*, %): 530 (100) [M]⁺. Calcd. for C₃₃H₂₇N₂O₃P: C, 74.71; H, 5.13; N, 5.28. Found: C, 74.60; H, 5.01; N, 5.36.

Diphenyl [{1, 1'-biphenyl-4-ylamino} (3-nitrophenyl) methyl] phosphonate (4j)

Yellow solid, yield 90%, m.p: 169-171 °C. IR: 3415 (NH), 1235 (P=O), 747 (P-C_{aliphatic}); ¹H NMR: 4.87 (t, 1H, *J*= 20.5 Hz, NH), 5.82 (dd, 1H, *J*=16.2 Hz, *J*=9.8 Hz, P-C-H), 7.19-8.14 (m, 23H, ArH); ¹³C NMR: 58.5 (C₄), 113.5 (C₂₇,C₃₁), 115.3 (C₁,C₈,C₁₂,C₁₇), 120.7 (C₁₀,C₁₉), 121.5 (C₂₄), 122.4 (C₂₂), 124.7 (C₂₉), 127.1 (C₃₃,C₃₇,C₃₅), 128.3 (C₂₈,C₃₀), 129.5 (C₃₄,C₃₆), 129.8 (C₉,C₁₁,C₁₈,C₂₀), 131.5 (C₂₆), 136.2 (C₃₂), 140.2 (C₂), 145.1 (C₁₃), 147.2 (C₂₁), 155.7 (C₇,C₁₆); ³¹P NMR: 22.1, LC-MS (*m/z*, %): 537 (100) [M+H]⁺. Calcd. for C₃₁H₂₅N₂O₅P: C, 69.40; H, 4.70; N, 5.22. Found: C, 69.33; H, 4.63; N, 5.33.

Anti-microbial assays

The titled synthesized compounds were dissolved in DMSO at concentrations of 150, 250, and 350 μg/mL.

Anti-bacterial and anti-fungal assays

Preliminary anti-microbial activities of the titled compounds were tested by agar disc-diffusion method.²⁵

Anti-oxidant assay

Evaluation of anti-oxidant activity was done by using the 2, 2'-diphenyl-1-picrylhydrazyl (DPPH) method.²⁶

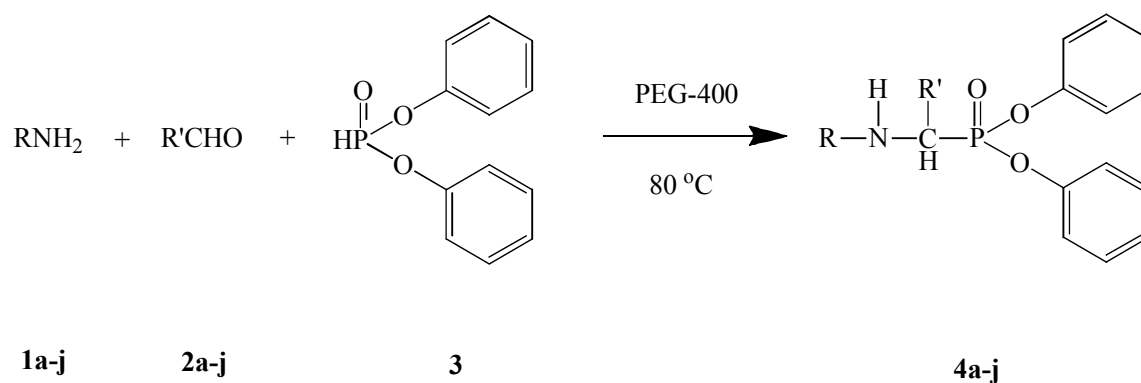
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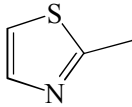
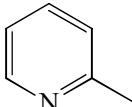
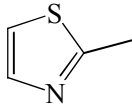
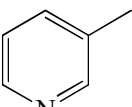
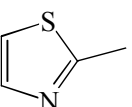
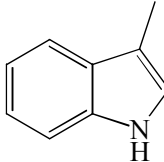
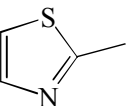
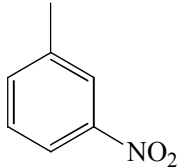
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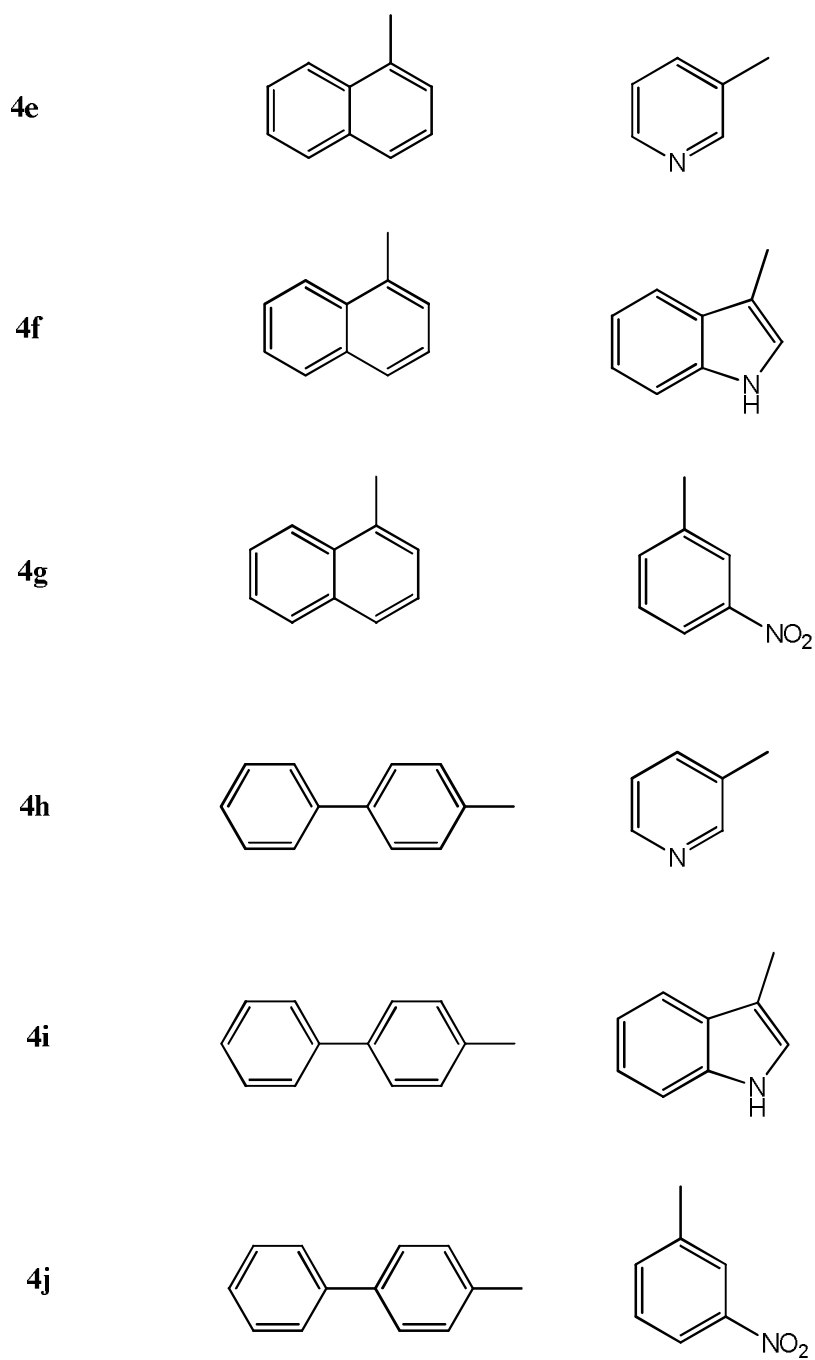
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Compound	R	R'
4a		
4b		
4c		
4d		



Scheme 1. Synthesis of novel α -Aminophosphonates (**4a-j**)

ON DOMINATION OF FUZZY GRAPHS AND FUZZY TREES

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Abstract

The object of this paper is to generalize the dominations in fuzzy graphs. In this paper we discuss the concept of edge domination, total edge domination in fuzzy graphs. Further we extend to vertex edge domination and perfect vertex (edge) domination in operations of fuzzy graphs, observe the disparity between strong (weak) dominations and equitable domination in fuzzy graphs. In this paper we extended our study to domination in fuzzy trees and derived some results related to the above dominations in fuzzy graphs and prompt some applications on them like as traffic light problems, networking problems, transportation and banking services

AMS Subject Classification: 05C75

Key Words and Phrases: Total edge domination, perfect vertex (edge) domination, strong (weak) and equitable dominations in fuzzy graphs and fuzzy trees.

1 Introduction

One of the notable mathematical inventions of the 20th century is that of Fuzzy sets by Lotfi. A. Zadeh in 1965. His aim was to develop a mathematical theory to deal with uncertainty and imprecision. The advantage of replacing the classical sets by Zadehs fuzzy sets is that it gives more accuracy and precision in theory and more efficiency an system compatability in applications[1]. The distinction between the set and fuzzy set is that the set divide the universal set into two subsets, namely members and non-members while fuzzy set assigns a sequence of membership values to elements of the universal set ranging from 0 to 1. Fuzzy graphs are useful to represent relationships which deal with uncertainty and it differs greatly from classical graph. The first definition of Fuzzy graph by Kaufman(1973) was based on Zadehs fuzzy relations (1971). After that Rosenfeld (1975) who considered fuzzy relation on fuzzy sets and developed the theory of fuzzy graphs.

Several works on fuzzy graphs are also done by Akram, Samanta, Dudek, Davvaz, Sunitha [2,4,5,7,12]. It was during 1850s a study of dominating sets in graphs started purely as a problem in the game of chess. Chess enthusiasts in Europe considered the problem of determining the minimum number of queens that can be placed on a chess board so that all the squares are either attacked by a queen or occupied by a queen. The study of domination set in graphs was begun by Ore and Berge. A. Somasundram and S. Somasundram[7] discussed domination in Fuzzy graphs. The edge domination was introduced by Mitchell and Hedetniemi. V.R. Kulli and D.K. Patwari[4] discussed the total edge domination number of graph. They defined domination using effective edges in fuzzy graph. The concept of Perfect domination was introduced by CoCkayne et al. Perfect edge domination in graphs was studied in [3]. Perfect k-domination in graphs was studied in [4]. Edge domination in fuzzy graphs was defined in [7]. A work on Fuzzy Multiple domination was done in [8]. The concept of equitable domination [11] in graphs was introduced by Venkata Subramanian Swaminathan and Kuppusamy Markandan Dharmalingam.

2 Preliminaries

It is known that graphs are simply models of relations. A graph is a convenient way of representing information involving relationship between objects. The objects are represented by vertices and relations, by edges. When there is vagueness in the description of the objects or in its relationships or in both, it is natural that we need to design a fuzzy graph model. Here we summarize some basic definitions of dominations in fuzzy graph.

Definition 2.1. Let V be a finite non empty set and E be the collection of two

element subsets of V . A fuzzy graph $G = (\sigma, \mu)$ is a set with two functions $\sigma : V \rightarrow [0, 1]$ and $\mu : E \rightarrow [0, 1]$ such that $\mu(x, y) \leq \min\{\sigma(x), \sigma(y)\}$ for all $x, y \in V$. The order p and size q of a fuzzy graph $G = (\sigma, \mu)$ are defined to be $p = \sum \sigma(x)$, where $x \in V$, and $q = \sum \mu(xy)$ where $xy \in E$.

Definition 2.2: Let $G = (\sigma, \mu)$ be a fuzzy graph on V and $S \subseteq V$. Then the fuzzy cardinality of S is defined to be $\sum \sigma(v)$ where $v \in S$.

Definition 2.3: Let $G = (\sigma, \mu)$ be a fuzzy graph on D and $D \subseteq E$ then the fuzzy edge cardinality of D is defined to be $\sum \mu(e)$ where $e \in D$.

Definition 2.4: An edge $e = xy$ of a fuzzy graph is called an effective edge if $\mu(xy) = \sigma(x) \wedge \sigma(y)$. $N(x) = \{y \in V / \mu(xy) = \min\{\sigma(x), \sigma(y)\}\}$ is called the neighborhood of x and $N[x] = N(x) \cup \{x\}$ is the closed neighborhood of x .

3 Domination in Fuzzy Graphs

Definition 3.1: Let $G = (\sigma, \mu)$ be a fuzzy graph on (V, X) . A subset S of X is said to be an edge domination set in G if for every edge in $X - S$ is adjacent to at least one effective edge in S . The minimum fuzzy cardinality of an edge domination set G is called the edge domination number of G and its denoted by $\gamma'(G)$ or simply γ' .

Example:

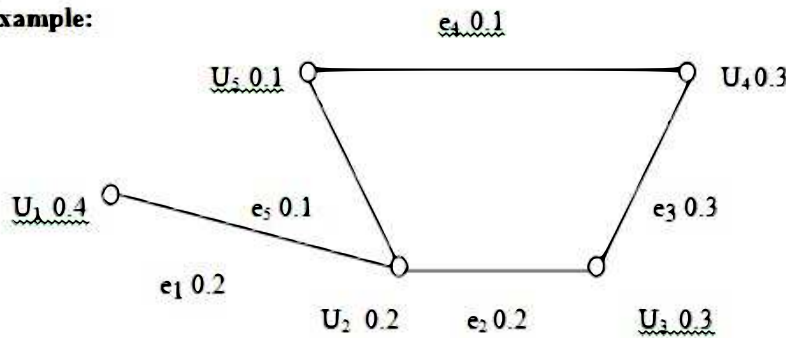


Figure 1:

For the fuzzy graph in figure 1. $S = \{e2, e4\}$, $X - S = \{e1, e3, e5\}$, Edge domination number of the above fuzzy graph is $\gamma'(G) = 0.3$.

Definition 3.2: An edge e of a fuzzy graph G is said to be an isolated edge if no effective edges Incident with the vertices of e . Thus an isolated edge does not dominate any other edge in G .

Corollary 1. For any fuzzy graph G without isolated edges $\gamma' \leq q/2$.

Proof. Any graph without isolated edges has two disjoint edge dominating sets and hence the result follows. \square

Theorem 2. *If G is a fuzzy graph without isolated edges, then $q / [\Delta \gamma(G) + 1] \geq \gamma \gamma(G)$.*

Proof. Let D be an edge dominating set of G.

$$\begin{aligned} \text{Since, } |D| \Delta \gamma(G) &\leq \sum d(e) = \sum |N(e)| \text{ where } e \in D \\ &\leq \cup N(e) \text{ where } e \in D \\ &\leq |E - D| \\ &\leq q - |D| \end{aligned}$$

$$\begin{aligned} \text{Hence } |D| \Delta \gamma(G) + |D| &\leq q \\ |D| \Delta \gamma(G) + 1 &\leq q \\ \text{Thus } \gamma \gamma &\leq q / [\Delta \gamma(G) + 1] . \end{aligned}$$

\square

Definition 3.3: Let G be a fuzzy graph without isolated edges. A subset D of E is said to be a total edge dominating set, if every edge in E is dominated by an edge in D. The minimum fuzzy cardinality of a total edge dominating set is called the total edge domination number of G and it is denoted by $\gamma \gamma_1(G)$.

Definition 3.4: An edge dominating set X of a fuzzy graph G is said to be a perfect edge dominating set if every edge of E-X is adjacent to exactly one edge in X. The perfect edge dominating set X of a fuzzy graph G is said to be a minimal perfect edge dominating set if for each edge $uv \in X$, X - (u, v) is not a perfect edge dominating set. The cardinality of a minimum perfect edge domination set is called as perfect edge domination number and is denoted by

Example:

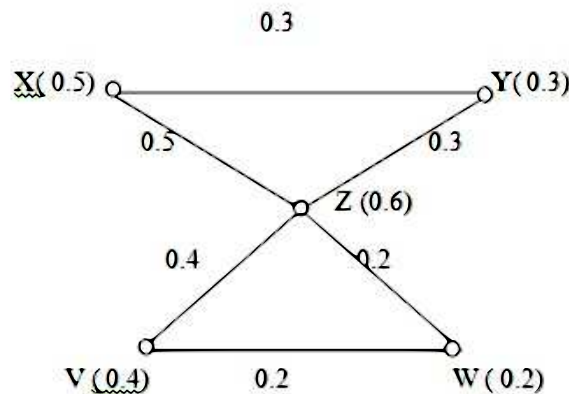


Figure 2:

In the above graph the edge dominating set is given by $\{VW, YZ\}$. $\gamma'(G) = 0.5$. But it is not a perfect edge dominating set.

The perfect edge dominating set is given by $\{XY, VW\}$, $\gamma(G) = 0.5$

Example:

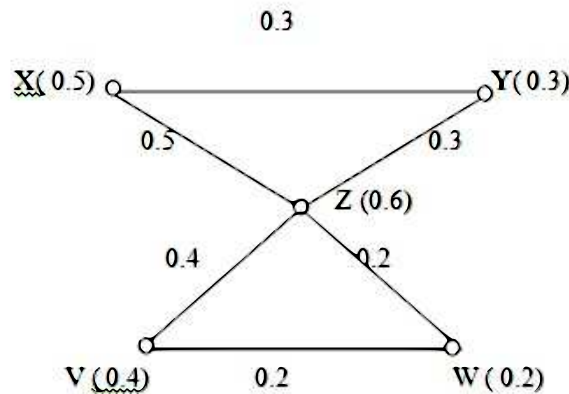


Figure 3:

In the Figure 3. The edge dominating set is $\{c d\}$ which is also a perfect edge dominating set. i.e., $\gamma'(G) = \gamma'_{PF}(G)$

Definition 3.5: According to Nagoor Gani[8] a node v in a fuzzy graph G is said to strongly dominate itself and each of its strong neighbors, that is, v strongly dominates the nodes in $Ns[v]$. A set D of nodes of G is strong dominating set of G if every node of $V(G) - D$ is a strong neighbor of some node in D . They defined a minimum strong dominating set in a Fuzzy graph G as a strong dominating set with minimum number of nodes.

Definition 3.6: The weight of a strong dominating set D is defined as $W(D) = \sum (u,v)$. Where (u, v) is the minimum of the membership values (weights) of the strong arcs incident on u . The strong domination number of fuzzy graph G is defined as the minimum weight of strong dominating sets of G and it is denoted by $\gamma_s(G)$. A minimum strong dominating set in a fuzzy graph G is a strong dominating set of minimum weight.

In this fuzzy graph strong arcs are (u, w) , (w, x) and (x, v) . The minimum strong dominating sets $D1 = \{u, x\}$ and $D2 = \{w, x\}$. Where $W(D1) = 0.2 + 0.3 = 0.5$ and $W(D2) = 0.2 + 0.3 = 0.5$ Hence $\gamma_s = 0.5$

Corollary 3. In any fuzzy graph $G : (V, \sigma, \mu)$, $\gamma(s) \leq p$ always holds, since $(x,y) \leq \min \{\sigma(x), \sigma(y)\}$ for all $x, y \in V$, where γ_s is the weight of the minimum strong dominating set, which is got by using the arc weights.

Example:

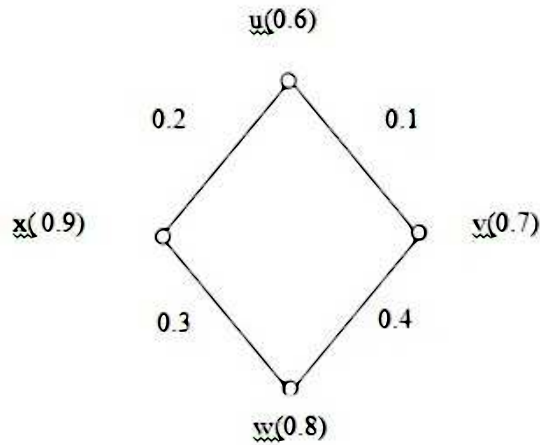


Figure 4:

Theorem 4. For any connected fuzzy graph $G : (V, \sigma, \mu)$ of order p .
 $\min \mu (u, v) \leq \gamma_s \leq p - \Delta_{SN} (G)$.

Proof. The first part is trivial. For the second part, let u be a node of G such that $D_{SN}(u) = \Delta_{SN} (G)$. Then $V - N_S (u)$ is a strong dominating set. Therefore, $\gamma_s \leq W (V - N_s (u)) \leq p - \Delta_{sN} (G)$.
 Therefore, $\gamma_s \leq p - (G)\Delta_{SN} (G)$ □

4 Domination in Fuzzy Trees

Definition 4.1: A Tree is a connected graph containing no cycle. A tree is composed by nodes, which are linked by edges such that there exists a particular node called root and such that all the nodes but the root are composed by sub trees.

Definition 4.2: A graph without cycles is called an acyclic graph (or) forest. A linked forest on which all nodes are linked is called a tree. A fuzzy graph can be defined as a forest if a graph, which contains all its arcs, takes the shape of a forest. An undirected fuzzy graph can be defined a tree if a graph, which contains all its arcs, takes the shape of a linked forest.

Definition 4.3: Let $T (\sigma, \mu)$ be a fuzzy tree on (V, E) . A subset D of E is said to be an edge domination set in T if for every edge in $E - D$ is adjacent to at least one effective edge in D . The minimum fuzzy cardinality of an edge domination tree T is called the edge domination number of T and is denoted by $\gamma_l (T)$.

In the above example bc, bd is an edge dominating set in the given rooted fuzzy

Example:

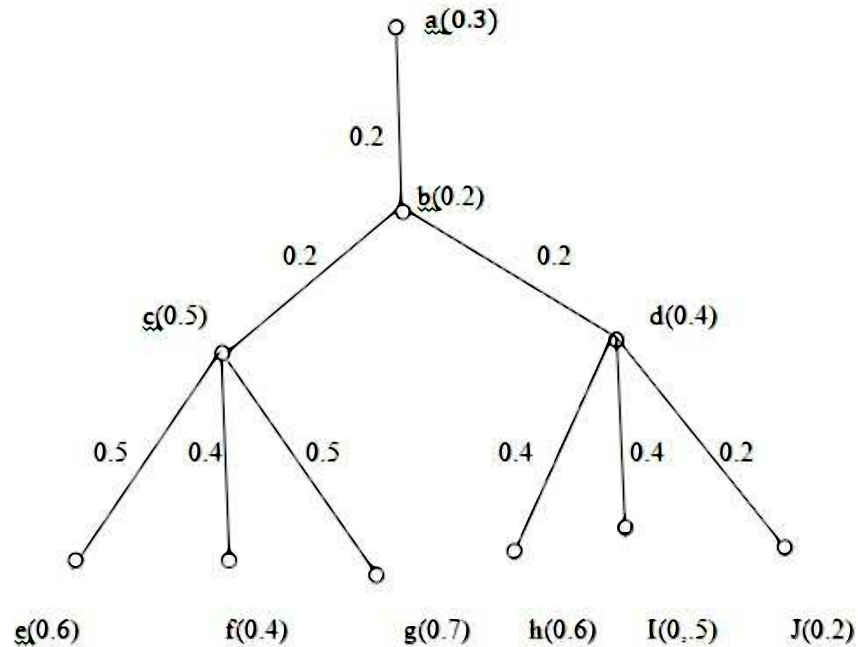


Figure 5:

tree.

Theorem 5. *A graph is a fuzzy tree if and only if it is minimally connected.*

Proof. Let the fuzzy graph $G(v, \sigma, \mu)$ minimally connected. Then $G(v, \sigma, \mu)$ has no cycles and therefore is a fuzzy tree $T(\sigma, \mu)$. Conversely, let T be a fuzzy tree. Then the fuzzy graph $G(v, \sigma, \mu)$ contains no cycles, and deletion of any edge from fuzzy graph G disconnects the graph. Hence fuzzy graph $G(v, \sigma, \mu)$ is minimally connected. \square

5 Applications:

The application of domination in fuzzy graph lies in various fields in solving real life problems. It includes social network theory, land surveying, radio station computer communication networks, school bus routing sets of representatives, interconnection networks etc. The online social network has been developed significantly in the recent years as a medium of communication, sharing the information and spreading

the influence. The dominating set plays a vital role in analyzing the effect on a real online social network data set through simulation. The dominating set concept can be applied to the social network graph to determine the amount of positive influence that is possessed by an individual as well as its impact to their related neighbor. An undirected graph $G = (V, E, C)$ is used to denote the online social network, because friendship in an online social network are usually bidirectional. Online social network can be represented as a graph of relationship with individuals representing the nodes of a graph (V), the social interactions as edges (E) and C is the compartment vector that saves the compartment of each node. The compartment part of a node decides whether the social issues of an individual has positive or negative impact on his neighbours.

6 Dominating set in Mobile Ad-hoc Network:

A Mobile Ad-Hoc Network is as configurable infrastructure less network connecting the mobile devices in wireless mode. The dominating set has been commonly used for routing and broadcasting the information to the mobile devices in mobile ad-hoc networks. The connected dominating set is widely used as a virtual backbone for Mobile Ad-hoc network is to provide different communication primitive such as routing, broadcasting etc.

7 Conclusion:

The concept of domination in graph is very rich both in theoretical developments and applications. More than thirty domination parameters have been investigated by different authors, and in this paper the concept of domination in trees has been adapted for fuzzy graphs using the membership values of strong arcs.

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