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3. Palmer, J.D. 1992. In Cell Orgenelles (R.G. Herman, Editor) Springeru Verlag, Vienna, 99.133.
4. Weber, D.R. 1967. On the Interaction of Nonhomologous Segments of Chromosomes in Zea mays. Unpubl. Ph.D. Thesis, Indiana University, Bloomington, Indiana, USA. (For Indian Universities, Country's name not to be indicated).
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A REVIEW ON SPOILAGE OF PACKAGED FOOD PRODUCTS BY BACTERIA

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ABSTRACT

Food deterioration is a significant problem in the food industry. Due to microorganisms, tons of food is currently contaminated. The origins of these microorganisms include water, soil, humans, machinery, and food packaging. Initially, these microorganisms do not exist in food. Bacteria play a significant role in food spoilage, thereby rendering food unsuitable for human consumption. If food packaging is not done properly, food spoilage becomes a significant concern. Different varieties of packaging are required for various foods to prevent microbial contamination. This article will discuss the various forms of food packaging and the bacterial spoilage of packaged foods. In addition, we will discuss the mechanisms by which different categories of food are spoiled by bacteria. The preservation of foodstuffs has been essential for human survival. Without any knowledge of microbiology, the earliest food preservation techniques relied on the inactivation of bacteria and fungi responsible for food deterioration. Typically, food items were preserved from microorganisms through dehydrating, salting, heating, chemical preservatives, or fermentation. In order to prevent the proliferation of microorganisms that cause food to spoil, a variety of food preservation techniques and combinations thereof are employed. Microbial food degradation was characterized by the sensory alteration of food products that renders them unacceptable to the consumer. Food spoilage can be caused by physical damage, chemical changes (oxidation and color changes), or a change in flavors and odors induced by microbial growth and metabolism in the food products. The most prevalent cause of food spoilage is microbial growth in food substance, which manifests as visible growth (slime, colonies), textural changes (polymer degradation), or off-odours and off-flavors.

Key Words: Bacteria, Spoilage, Packed Food Products.

INTRODUCTION

It is nearly impossible to envision food without a package in today's society. Food and packaging are inseparable. Whether it is farm-fresh cereals, food from a processing plant, or simply cow's milk, food packaging is ubiquitous (Gupta et al., 2017). Packaging has become such an integral component of food production that it serves as a link between the manufacturer and the consumer (Rangarao, 2005). It safeguards food against contamination caused by the environment and other factors (such as fragrances, shocks, dust,

temperature, physical damage, light, microorganisms, and humidity). It is essential for assuring the quality and safety of food, extending its shelf life, and reducing food waste (Qien & Yang, 2017).

One of the most essential aspects of a food's journey from farm to fork is its packaging, not the food itself. However, food packaging also has negative effects. Almost 25 percent of food spoilage is due to improper packaging. Food spoilage is a metabolic process in which the food becomes unfit or unsuitable for human ingestion.Food spoilage due to microbes occurs when an unwelcome microorganism is present in the manufactured food, rendering it unsuitable for consumption (Petruzzi et al., 2017; Houghton,2016).Due to the migration of substances from the packaging into the food, packaging has been identified as a major source of contamination in recent years. Numerous microorganisms, including bacteria, play a significant role in spoilage and cause severe problems. When microbes break down food, they produce acids and other waste products (Tull, 1997).These waste products are foul-tasting and potentially hazardous (Trickett, 2001). Appropriate packaging is required to preserve the fundamental characteristics of food, such as color, flavor, temperature, and texture. The primary purpose of packaging is to ensure food safety. Consequently, it is crucial that the packaging material be of high quality and safety (Gupta et al., 2017).

Escherichia coli, Pseudomonas aeruginosa, Staphylococcus aureus, Listeria monocytogenes, Campylobacter jejuni, Yersinia enterocolitica, and Salmonella typhi have been reported as some of the most prevalent pathogenic microorganisms in the dairy industry that are associated with food borne diseases, food borne diseases, and food borne intoxification. This microorganism is a short filament capable of thriving in both aerobic and microaerophilic environments. The optimal temperature for growth of microorganisms that cause decomposition in dairy products is 35 to 37 °C, but some spoilage-causing organisms can grow at refrigerated temperatures, over a wide pH range of 4 to 9 with salt concentrations up to 10%. Although the dairy industry is most concerned about the presence of Listeria monocytogenes in cheese, yoghurt, raw milk, and curd (Jageethadevi et al., 2012; Savitha Janakiraman et al., 2012), Listeria monocytogenes has been found in other dairy products as well.

The use of chemical preservatives and organic acids currently employed to control the dairy product spoilage-causing microorganisms that are capable of growing in milk products, such as sulphites, sulphur dioxide, sodium chloride, phosphates, hydrogen peroxide, nitrates, nitrites, sodium diacetate, citric acid, acetic acid, lactic acid, benzoic acid, fumaric acid, and therapeutic antibiotics, is being increasingly questioned These types of inquiries challenge the food processing and manufacturing industries to concentrate on natural methods of food preservation because food service customers demand high-quality products with a relatively long shelf life, but still prefer the appearance of minimally processed dairy food products (Hugas et al., 2002; Ross et al., 2002).

A number of microorganisms belonging to the Lactobacillus genus are able to produce biologically active antimicrobial peptides, also known as bacteriocins, which have broad-spectrum activity, a mode of action that achieves the target, the appropriate molecular weight, and specific biochemical properties.

Bacteriocins are bacteriostatic or bactericidal to pathogenic bacteria, particularly those that are closely related taxonomically, as well as food spoilage-causing bacteria. Typically, the producer strain is resistant to the bacteriocin it produces (Abee et al., 1995; O'Keeffe et al.,

1999; Van Reenen et al., 2002).

Bacteriocins produced by food-associated microorganisms such as lactic acid bacteria, specifically Lactobacillus lactis and Lactobacillus acidophilus, are gaining increasing interest as food biopreservatives (Abee et al., 1995). Bacteriocins are readily degraded by the protein-degrading enzyme protease in the human gastrointestinal tract due to their protein nature, and the majority of bacteriocin-producing lactic acid bacteria have GRAS status. Bacteriocins are regarded as natural biopreservatives for this reason (Schillinger et al., 2001; Aymerich et al., 2000). Bacteriocins may also be used as part of a multiple hurdle preservation system (Cleveland et al., 2001), and the bacteriocin produces may be applied as bacteriocinogenic cultures to non-fermented foods or even be used as starter culture for fermented foods to improve quality and safety and control bacterial spoilage or pathogenic bacterial isolates (Zhang et al., 1999; Nilsson et al., 2000).

Various researchers have reported a variety of bacteriocin activities and suggested its potential in the food industry (Cleveland et al., 2001). However, it was necessary to conduct applied studies to confirm the efficacy of the addition of bacteriocins to food systems, as it has been demonstrated that bacteriocins are not effective in all food systems (Ganzle et al., 1999; Cleveland et al., 2001). Patented applications of bacteriocins as food preservatives include the use of a combination of nisin (produced by Lactococcus lactis subsp. Lactis and Lactobacillus acidophilus), a chelating agent and a surfactant to inhibit the growth of both Gram positive and Gram negative pathogenic microorganisms in various dairy products like milk, cheese, butter, butter milk, ghee and yoghurt (Blackburn et al., 1998). In combination with a chelating agent, Streptococcus and Pediococcus-derived bacteriocins were used successfully to protect dairy food products against Listeria monocytogenes and other milk spoilage-causing microorganisms (Wilhoit, 1996).

VARIATIONS IN FOOD PACKAGING

Today, food packaging is a significant industry that employs tens of thousands of people. Choosing an appropriate and suitable material for food packaging is directly proportional to the functions that the product must perform. This includes protecting food from moisture, temperature fluctuations, oxygen, light, and microorganisms. In addition to damage resistance, permeability, food identification, and chemical and optical properties, the selection of the material is heavily influenced by other factors (Siracusa et al., 2018).

BASIC MECHANISM OF FOOD SPOILAGE

The initial and most important stage in food spoilage is bacterial contamination. This includes the attack of microbes on food from various internal or external sources. These bacteria may already be present in the food or may infiltrate from the outside. After the process of contamination, these food-spoiling microorganisms release enzymes that degrade food components. This breakdown of food components typically initiates the decomposition process. Bacteria utilize food constituents including carbohydrates and sugars. These nutrients are bacteria's dietary source. Enzymes from bacteria begin to interact with dietary components. These enzymes and dietary components like lipids, proteins, fats, vitamins, carbohydrates, etc. undergo enzymatic reactions.This results in food spoilage. As food begins to degrade, acids and other waste products are produced. A few hours or days later, the food product begins to

decompose. This food decomposition results in numerous chemical alterations. Degradation of carbohydrates, decomposition of N-compounds, decomposition of lipids, and hydrolysis of pectin are these chemical changes (Chavan, 2019).

As the process continues, changes in texture, color, and odor begin to occur. The chemical transformations inevitably result in a disagreeable flavor and taste. These alterations ultimately result in food deterioration. Food that has become unsuitable for human consumption must be discarded. This results in dietary loss.

PREVENTION FROM FOOD SPOILAGE

As a result of the substantial amount of food that is lost due to deterioration and contamination, the need for food preservation increases dramatically. As food products are now distributed globally, it is necessary to increase their shelf life. Additionally, numerous preservatives are added to the food to extend its expiration life and prevent spoilage. Included among these are acetic acid, ascorbic acid, lactic acid, and benzoic acid. These inhibit bacterial cell proliferation.

Additionally, numerous chemical preservatives are applied to inhibit microbial activity such as fermentation and decomposition. Among these are table salt, vinegar, sugar, etc. Most commonly, sodium benzoates are added to citrus juices. Food additives are utilized as well. Packaging plays a significant function in food preservation as well. Active packaging, intelligent packaging, and Ultimate packaging are examples of various forms of packaging.

Active packaging enhances the packaging system and controls the development of microorganisms and the migration of moisture. These contribute significantly to food preservation. Its applications include oxygen absorption, CO2 emission, antimicrobials, moisture control, and ethylene absorption.

Intelligent packaging examines various aspects of the food product. It increases the product's value. It includes time-temperature indicators (TTIs), indicators of ripeness, biosensors, and radio frequency identification. Occasionally, there are also leak indicators and pathogen indicators (Rajesh et al., 2020).

DISCUSSION

Borch et al. (1996) define spoilage of dairy products as the presence of a specified maximum microbial level or an objectionable off-flavor, off-odour, or appearance, or a change in the nature of the food. Escherichia coli, Listeria monocytogenes, Pseudomonas aeruginosa, Campylobacter jejuni, Yersinia enterocolitica, and Staphylococcus aureus are microorganisms that frequently cause food-borne diseases and food-borne poisoning linked to dairy products. Listeria monocytogenes, on the other hand, is a psychrotrophic food-borne pathogen that grows swiftly at refrigeration temperatures and is typically found in dairy products (Abee et al., 1995). Staphylococcus aureus-related food poisoning causes severe symptoms and is typically associated with dairy products. In this instance, food poisoning is caused by the presence of a toxin in the contaminated food and dairy products (Kennedy et al., 2000).

Bacteriocin from Lactobacillus lactis culture was examined for its effect on Listeria monocytogenes, Yersinia enterocolitica, Campylobacter jejuni, Staphylococcus aureus, and Pseudomonas aeruginosa. With an increase in culture bacteriocin concentration from 20 to 100 g ml-1, the diameter of the inhibition zone for all bacterial strains increased. Listeria monocytogenes exhibited the greatest zone of inhibition (23.00 mm), followed by Staphylococcus aureus (22.00 mm), Yersinia enterocolitica (20.00 mm), and Pseudomonas aeruginosa (18.66 mm).

Campylobacter jejuni had the smallest zone of inhibition (19.33 millimeters). Numerous scientists hypothesized that lactic acid bacterial isolates, such as Lactobacillus lactis and Lactobacillus acidophilus, possess antagonistic activity against infectious pathogens.

Ogunbanwo (2008) proposed that the lactic acid bacteria Lactobacillus acidophilus isolated from milk products and their study was based on its ability to produce a bioactive protein bacteriocin with inhibitory activity against food spoilage and food borne pathogenic bacteria such as Staphylococcus aureus, Listeria denitrificans, Listeria monocytogenes, Campylobacter jejuni, Yersinia enterocolitica, Pseu

Lactic acid bacteria like Lactobacillus lactis and Lactobacillus acidophilus isolated from various milk products were able to inhibit the growth of Bacillus cereus, Bacillus subtilis, Staphylococcus aureus, Micrococcus luteus, Listeria monocytogenes, and Gram negative bacteria including Escherichia coli, Pseudomonas fragi, Pseudomonas aeruginosa,

Kanatani et al. (1995) reported that Lactobacillus acidophilus strains possess biopreservative properties. They found that Lactobacillus acidophilus produced bacteriocin that was effective against various species of Enterococcus casseliflavus, Lactobacillus lactis, Lactobacillus acidophilus, Pediococcus sp., Streptococcus pyogenes, and Listeria monocytogenes. Vaccination with Listeria

Monocytogenes in dairy products can be used as a starter culture to prevent the proliferation of microbes that cause milk products to degrade when exposed to high temperatures.

The effect of time and temperature on the thermal stability of crude bacteriocin (extracted from Lactobacillus lactis and Lactobacillus acidophilus) on the inhibition of dairy product spoilage bacteria was investigated. The inhibitory activity was unaffected by heating at 120 oC for 40 minutes, and 70% of activity was retained following a 15-minute heating at 120 oC. More inhibition was observed at 20 oC after 15 minutes, followed by 40 oC, 60 oC, 80 oC, 100 oC, and 120 oC. The activity of crude bacteriocin in Lactobacillus acidophilus and Lactobacillus lactis after 15 minutes of heating at 121 degrees Celsius, as reported by Savitha Janakiraman et al. in 2012, decreased after heating at 121 degrees Celsius. Therefore, it could be classified as a heat-stable bacteriocin with a low molecular weight. The results of the present study were consistent with those proposed by Savitha Janakiraman et al. (2012).

The effect of surfactant on the stability of crude bacteriocins from Lactobacillus lactis and Lactobacillus acidophilus against bacteria that cause the deterioration of dairy products was investigated. Among the numerous surfactants at concentrations of 0.2%, 0.4%, 0.6%, 0.8%, and 1%, HDTMEB exhibited the greatest inhibitory activity against dairy product spoilage bacteria, followed by SDS, EDTA, TWEEN 80, and TWEEN 20. According to Savitha Janakiraman et al. (2012), the incorporation of non-

Ionic detergents such as SDS, EDTA, TWEEN 20, and TWEEN 80 substantially decreased the bacteriocin activity of Lactobacillus acidophilus and Lactobacillus acidophilus, whereas the cationic detergent hexadecyl trimethyl ammonium bromide enhanced the crude bacteriocin activity.

At 5 mg/L, 10 mg/L, 15 mg/L, 20 mg/L, and 25 mg/L, the inhibitory effect of metal ion on crude bacteriocin on Lactobacillus lactis and Lactobacillus acidophilus against dairy product spoilage bacteria was investigated. It was observed that the diameter of the inhibition zone decreased as the metal ion concentration rose. Copper sulphate displayed the greatest inhibitory effect against Listeria

monocytogenes at a concentration of 5 mg/L, followed by Ferrous sulphate, Calcium chloride, Zinc sulphate, and Mercuric chloride. Savitha Janakiraman et al. (2012) reported that as the concentration of metal ion increased, the activity of crude bacteriocin produced by Lactobacillus acidophilus and Lactobacillus acidophilus decreased. Graciela et al. (1995) observed a similar phenomenon in the culture filtrate of Lactobacillus casei.

CONCLUSION

Packaging extends the expiration life of food and preserves its quality and flavor. Due to the absence of packaging, bacteria can develop and establish themselves in a variety of culinary products. It has the potential to contaminate numerous foods, including milk, meat, fish, fruits, and vegetables. The processing environment and packaging type have a significant impact on food deterioration. To ensure food safety and quality, packaging, storage, and distribution of food should be performed meticulously. Therefore, appropriate packaging is necessary to preserve the integrity of food, and it is also essential that the packaging material be food-grade. Bacteria multiply and cause a variety of food deterioration issues. This has been a significant problem for humanity for centuries. Diverse techniques and methods are being developed and utilized to prevent food from spoiling. Science has developed numerous packaging techniques and preservatives to prevent food from spoiling. Nanotechnology is presently being used to create the ultimate packaging, but it has not been widely adopted.

REFERENCES

1. Abdullahi AA, Bala JD, Kuta FA, Adabara NU, Liyasu USet al. 2020.A review on Microbial Spoilage of Food in Industry. FUW Trends in Science & Technology Journal. 4(2): 519-523.
2. Barth M, Hankinson TR, Zhuang H & Breidt F 2009. Microbiological spoilage of fruits and vegetables.Compendium of the Microbiological Spoilage of Foods and Beverages.Pp. 135-183.
3. David Beltran, Maria VS, Juan A & Maria IG. 2005. Effect of different sanitizers on microbial and sensory quality of fresh-cut potato strips stored under modified atmosphere or vacuum packaging. Postharvest Biology and Technology. Pp.37-46.
4. BPF.2013. British Plastic Federation.Plastic Packaging: The Progressive Packaging Medium.
5. Chavan UD. 2019. Biochemistry of Food Spoilage. In: MTC Training Course.
6. Doyle ME. 2007. Microbial Food Spoilage-Losses and Control Strategies: A Brief Review of the Literature. Food Research Institute Briefings. University of Wisconsin–Madison.
7. Fellows, Peter. 2016. Food processing technology: principles& practice (4th ed.). Kent Woodhead Publishing/Elsevier Science.
8. FrancoI& Falque E. 2016. Glass Packaging. Reference Module in Food Science.
9. Geueke B, Groh K &Muncke J. 2018. Food Packaging in the circular economy: Overview of chem. safety aspects for commonly used materials. Journal of Cleaner Product.193:491-505.
10. Grayhurst P &Girling PJ. 2011. Packaging of food in glass containers. In: Coles R, Kirwan M (Eds.), Food and Beverage Packaging Technology, 2nd edition. John Wiley & Sons Ltd, UK.
11. Gupta RK & Dudeja P. 2017. Food packaging. 10.1016/B978-0-12-801773-9.00046-7.
12. Houghton M. 2016. Food Spoilage. Retrieve from Https://www.cliffsnotes.com/study-guides/biology/microbiology/food-microbiology/food-spoilage.
13. Jia-Wei Han, Luis-Ruiz-Garcia, Jian-Ping Qian, & Xin- Tin Yang. 2018. Food packaging: A Comprehensive Review & Future Trends. Comprehensive Reviews in Food Science and Safety. 17:860-877.
14. Mills J, Donnison A, Brightwell G.2014. Factors affecting microbial spoilage & shelf-life of vacuum-packed lamb transported to distinct markets: A review.Meat Science. 98(1):71-80.
15. Mohanty F & Swain SK. 2017. Bionanocomposites for Food Packaging Applications. Nanotechnology Applications in Food. 363-379.
16. Petruzzi L, Corbo MR, Sinigaglia M & Bevilacqua A. 2017. Microbial spoilage of foods: Fundamentals. In The Microbiological Quality of Food. Woodhead Publishing, pp. 1-21.
17. Rajesh G, Balasubramanian S, Manimehalai N & Anand, T. 2019. Food Packaging Technology. Everyman's Science. 54(3):180-186.
18. Shaw R. 2013. Food Packaging: 9 Types & Differences explained. Assemblies Unlimited.
19. Ray B & Bhunia A. 2013. Fundamental Food Microbiology. CRC Press.

20. Risch SJ. 2009. Food Packaging History & Innovations. Journal of Agricultural & Food Chem.,57(18): 8089- 8092.
21. Rawat S. 2015. Food Spoilage: microorganisms & their prevention. Asian J. Plant Sci.Res. 5(4):47-56
22. Siracusa V & Rosa MD. 2018. Sustainable Packaging. In Sustainable Food Systems from Agriculture to Industry. 275-307
23. Sun Dawen. 2011. Handbook of food safety engineering. Oxford: Wiley- Blackwell.
24. Urmila M, Poonam N, Shivani M & Kulvinder K .2017. A review on growth of different types of microorganism, intrinsic and extrinsic factors of microorganism and their affects in food. Int. J. Cur. Microbio. and Appl. Sci., 6: 290-298.

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A CRITICAL STUDY ON DEVELOPMENT OF NATURE-BASED SUSTAINABLE PASSIVE TECHNOLOGIES FOR TREATING AND DISINFECTING MUNICIPAL WASTEWATER

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ABSTRACT

In this era, disinfection and efficient effluent treatment are of critical importance. In this study, various types of constructed wetlands (CWs) followed by the biological slow sand filter (BSSF) were used on a larger scale than in the lab to treat and disinfect real municipal wastewater efficiently. As secondary wastewater treatment technologies, CWs with gravels (CW-G), free water surface (FWS-CWs), and CWs integrated microbial fuel cell (MFC) with granular graphite (CW-MFC-GG) were planted with Canna indica. In addition, tertiary treatment technology, BSSF for disinfection, was implemented. The combination of CW-MFC-GG-BSSF achieved the highest total coliform removal with a final concentration of 172 CFU/100 mL and 68.26% removal, whereas CW-G-BSSF and CW-MFC-GG-BSSF removed faecal coliform to an effluent concentration of 0 CFU/100 mL. In addition, faecal coliform E. coli was not detected in CW-G-BSSF and CW-MFC-GG-BSSF. In terms of treatment performance, CW-G-BSSF and CW-MFC-GG-BSSF attained low effluent COD concentrations in mg/L, respectively, with influent COD of 61.63 8.56 mg/L, as well as phosphate concentrations of 0.42 0.02 mg/L and 0.68 0.06 mg/L with influent phosphate concentration of 3. Consequently, the final effluent from both CW-G-BSSF and CW-MFC-GG-BSSF satisfies the discharge standards established by the Indian regulatory authority for both treatment and disinfection. CW-MFC-GG also demonstrated a power density of 85.71 mA/m3 and a current density of 25.71 mW/m3 in 48 hours at an internal resistance of 700. Therefore, CW-G and CW-MFC-GG followed by BSSF could be a promising approach for improved disinfection and wastewater treatment.

KEY WORDS: Nature, Sustainable, Technologies, Disinfecting Municipal Wastewater.

INTRODUCTION

In numerous arid regions of the globe, the agricultural sector's demand for water exceeds the available water resources on a temporary or permanent basis [2, 3]. Population growth and increasing demands are two of the most significant contributors to the deterioration of water scarcity. Consequently, this has led to a substantial increase in domestic water consumption, resulting in an enormous

quantity of effluent production. The Central Public Health and Environmental Engineering Organization (CPHEEO) estimates that 70-80% of domestically supplied water emerges as effluent [2, 3, 1].

To mitigate this issue, municipal wastewater that has been treated and reused for irrigation can be a viable alternative. However, the use of inadequately treated or untreated wastewater in irrigation fields is dubious due to the presence of undesirable levels of organics, turbidity, salinity, and, most significantly, pathogens originating from human feces. For unrestricted irrigation with the intention of raw consumption for crop feeding, the required levels of total/faecal/thermotolerant coliforms should be 1,000 colony-forming units (CFU)/100 mL [4], while European guidelines only permit E. coli loads of 200 or 100 CFU [9,3]. To accomplish these stringent discharge restrictions, a high-quality treatment of municipal wastewater prior to its reuse for agricultural purposes is essential. To achieve this objective, cost-effective technologies should be developed and chosen [3,6,8].

CWs are one of the conventional nature-based municipal wastewater treatment technologies. Subsurface flow CWs are extensively used as a secondary wastewater treatment technology and come in a variety of types. The majority of CWs are used to treat domestic and municipal effluent [5]. Alternatively, free water surface (FWS) CWs are extensively applicable for eutrophic lake/river remediation at the field level. Although its large land area requirement and sluggish treatment limit its use [4]. For the purpose of enhancing the efficacy of CWs, Microbial electrochemical technologies (METs) such as microbial fuel cells (MFCs) are merged with CWs to form the CW-MFC technology. In recent years, CW-MFCs have also acquired popularity due to their ability to improve wastewater treatment while simultaneously recovering electricity [23, 5]. Yadav [12] introduced CW-MFC as a stand-alone nature-based sustainable technology in 2010. The emergence of CW-MFCs was made possible by naturally occurring redox conditions in CWs [2, 6]. Importantly, CW-MFCs use conductive material as substrate rather than siliceous gravels (as in CWs), which can function as electron acceptors and donors in the oxygen-deficient/anaerobic and aerobic environments, respectively, thereby accelerating the microbial redox reactions [10,14, 17]. With time, CW-MFCs emerge as a promising technology for secondary effluent treatment, bioelectricity recovery, and numerous other applications.

The pathogen disinfection in CWs is primarily governed by vegetation and substrate, occurring either through (i) antibiotics or biocides secretion through its roots, (ii) attachment of microbes to the roots and filtration, (iii) physical processes such as attachment, sedimentation, adsorption, mechanical filtration through macrophyte roots, and filter materials, killing of microbes through ultra violet light of the sun's rays, or (iv) plant and Researchers found that effluent from CWs still contains excessively high levels of total coliform (TC), faecal coliform (FC), and E. coli (4 106, 9 105, and 3 103-2 106 CFU/100 ml for TC, FC, and E. coli, respectively) compared to the discharge standard, making effluent water unsafe for reuse [7, 6, 8]. As with other BES, some CW-MFC investigations have demonstrated the ability to produce strong oxidizing and disinfecting hydrogen peroxide (H2O2) on-site [9]. The maximum H2O2 yield was only 2.91 mg/L in CW-MFC operating under intermittent flow conditions with activated carbon as the filler substrate [10]. Overall, a post-disinfection step of secondary effluent obtained from CWs is required to attain pathogen-free effluent.

In this context, slow sand filters (SSF), a low-tech procedure, may be an effective method for disinfection and turbidity removal in drinking water purification [20] that has been used for decades. Where BSSF emerged as a promising wastewater remediation method that combines physical and biological processes. In continuous BSSF, water initially percolates slowly through the sand column due to the pressure of a constant water head. BSSF maintained this water level by installing the outlet conduit at a specific height. While sluggish percolation through the filter enables physical processes such as sedimentation, diffusion, and adsorption, large particles can be retained in the filter pore medium for organics removal. Simultaneously, biologically active components formed on the surface of the BSSF with continuous effluent flow and termed Schmutzdecke/dirt/hypogeal layer are responsible for the majority of pathogen removal. Schmutzdecke layer typically consists of bacteria, protozoa, rotifer, fungi, various aquatic insect larvae, alluvial mud, zooplanktons, diatoms, and thread-like algae forms as a result of microbial excretion, which facilitates pathogen removal via elimination, natural death/inactivation, predation, mechanical trapping, adsorption, etc. [11, 12, 13]. Overall, BSSF disinfection efficiencies for TC, FC, E. coli, and enterococci ranged from 0.3 to 3.5 log units, 2-2.4 log units, 1.9 to 4.1 log units, and 0.7 to 3.7 log units, respectively [14, 15, 16 , 17]. Therefore, BSSF could be an effective method for disinfecting secondary effluent for reuse.

Consequently, the current study investigates CW (non-conductive substrate), CW-MFC (conductive substrate), and free water surface CW (without substrate) as a secondary wastewater treatment technology followed by BSSF as a tertiary treatment step in an effort to improve the treatment and disinfection of actual municipal wastewater. According to the author's knowledge, this study is the first of its kind with the following objectives: (i) evaluation of pollutant performance efficiencies of planted upscaled CW-MFCs, CWs, and FWS CWs followed by BSSF for real municipal wastewater treatment; (ii) understanding how the TC, FC and E. Coli removal efficiencies can differ with different substrates and variable Canna indica vegetation growth in CW-MFCs, CWs and FWS CWs and, (iii) to ensure the final effluent received after BSSF treatment is safe for use in irrigation purposes.

MATERIALS AND METHODS

Experimental operation and sample collection

During the experiment, fed actual municipal wastewater after primary treatment to the microcosms. During the two-month acclimatization phase, microcosms were fed a 1:1 mixture of fresh wastewater and their own effluent. Acclimatization of microcosms was evaluated based on parameters such as the development of Canna indica vegetation, the stable voltage output of the CW-MFC-GG, and the consistency of microcosms' pollutant removal efficiencies. After the acclimatization phase concluded, microcosms were deemed suitable for further research.

Initially, 80 liters (L) of actual municipal wastewater was stored in a PVC tank to maintain and mix well in order to feed homogenous wastewater into the microcosms. Approximately 50 milliliters (mL) of influent wastewater was collected from the tank in a sample container. The initial working volume for each microcosm was determined as follows: 16.75 L (CW-G), 18.5 L (CW-MFC-GG), and 33 L (FWS). This hour (h) of microcosm filling was considered 0 h of batch loading; from this point forward, each microcosm undergoes the entire subsequent procedure at 8 h, 24 h, and

48 h intervals: (i) each microcosm was completely decanted, (ii) the decanted wastewater was homogeneously mixed for sample collection (volume collected: 50 mL), (iii) the decanted volume was measured for evaluation of evapotranspiration (ET) through each microcosm, and (iv) each microcosm was refilled with the decanted wastewater. After the conclusion of the rainy season, this 48-hour cycle was repeated weekly for six months, from September 2020 to February 2021. In addition, samples were stored at 4°C and analyzed for COD and phosphate on the second day after collection.

RESULTS AND DISCUSSION

Fabrication of upscaled microcosms

Three scaled-up microcosms of CWs were created using a cylindrical Linear low-density polyethylene (LLDPE) container measuring 60 cm x 32.5 cm (height x diameter) and maintained in natural environmental conditions. All of these containers came equipped with three sampling openings. The ports were provided from the top down, with the first port at 5.5 cm, the second at 33 cm, and the third at 57 cm. To ensure that every microcosm maintains an equal subsurface water level, the first port was left open for the duration of the investigation. Since microcosms were operated in bulk mode, the middle and bottom ports were utilized for sampling and decanting purposes. According to their configuration and filter substrate, three microcosms were designated as follows: CWs with garden gravel (CW-G), CW-MFC with granular graphite (CW-MFC-GG), and FWS-CW without a filter substrate. Each microcosm was seeded with Canna indica macrophyte from the CSIR-IMMT CW facility. Before being replanted in CW microcosms, the uprooted Canna indica sapling was rinsing with normal water five times. The average root length, shoot length, and weight were, respectively, 14.5 0.5 cm, 70 8 cm, and 200 70 g. Each uprooted Canna seedling had an average of two leaves prior to being transplanted into a microcosm. During the fabrication of the microcosms, large gravels with an average diameter of 20-25 mm were added to each microcosm up to a height of 10 cm from the bottom as a supporting layer, except for the FWS-CWs system, in which the large gravel layer was up to 14 cm to support the centrally located PVC pipe with a diameter of (diameter) = 20 mm on which Canna indica was supported for growth, as illustrated in Figure 1c. In addition, the center of each microcosm was fitted with a 20 mm diameter PVC conduit that served multiple purposes, including gas venting and water level measurement (evapotranspiration).

CW-G were filled with = 5-8 mm gravel on top of larger gravels to the top of the microcosm. In each microcosm, Canna indica was planted at a height of 15 centimetres from the top. CW-MFC-GG (Figure- 1a) was manufactured differently than CW-G (Figure-1b) due to the differentiation of the top and bottom layers and the embedding of the charge collector and dispenser. In CW-MFC, after the lining of a 10-centimeter layer of large gravels, a 15-centimeter layer of granular graphite (= 5-8 mm) was applied as an anode; a graphite plate with a surface area of 400.55 square centimeters was also inserted into this layer to serve as an electron collector. Subsequently, a 20 cm layer of normal gravel (= 5-8 mm) was utilized as a separator, which was enclosed by double lining of high-density polyethylene (HDPE) liner at both ends, followed by 15 cm of particulate graphite as a cathodic layer. In the cathodic layer, a 400.55 cm2 area electron dispenser was retained. To foster an oxygen-rich environment at the cathode, however, a portion of the (1.5 cm) cathode charge dispenser was elevated above the water level. Copper wire was used to connect the anode and cathode charge collector/dispenser, and epoxy was used to

encapsulate and insulate the exposed area. The resistance was connected to the remaining free extremities of the anode and cathode charge collectors/dispenser.

Biological slow sand filter assembly

As depicted in Fig. 1d, a BSSF with a 60 cm bed depth was constructed in an LLDPE container of 60 cm height and 31.5 cm diameter and equipped with three apertures located 4 cm, 27 cm, and 49 cm from the bottom. In the bottom segment of the BSSF unit, a 3.0 cm deep bed of large gravel (= 20-25 mm) was followed by a 3.0 cm deep bed of garden gravel (= 5-8 mm). The remainder of the BSSF unit was stuffed with river sediment. D10 (average particle diameter in mm) and D60 D10 uniformity coefficient (grain size distribution) for the river sand used in BSSF were 0.240 mm and 2.70 mm, respectively. In addition, the manufactured BSSF was continuously monitored and operated in a continuous mode for two months to acclimate the schmutzdecke layer. BSSF was fed effluent from CW-G, CW-MFC- GG, and FWS CWs microcosms that had been treated for 48 hours. Continuous operation of BSSF was achieved via drop-wise distribution of wastewater from the reservoir vessel (30 cm height, = 15 cm diameter) equipped with a tap. To maintain a flow rate of 116.7 mL/h, the reservoir was always filled to greater than 75 percent of its capacity. Since BSSFs operate in down flow motion, effluent pipe was siphoned from bottom port to maintain the water level above the top active schmutzdecke layer (promotes pathogen removal) and effluent pipe was further curved over the top port to allow discharge through gravity, as depicted in Figure 5-1d. The BSSF unit was utilized for 45 days to treat the effluent from each microcosm. The collected samples from the BSSF were analyzed further for treatment and disinfection in particular. Chemical oxygen demand (COD), phosphate, total coliform (TC), faecal coliform (FC), and E. coli were the parameters analyzed.

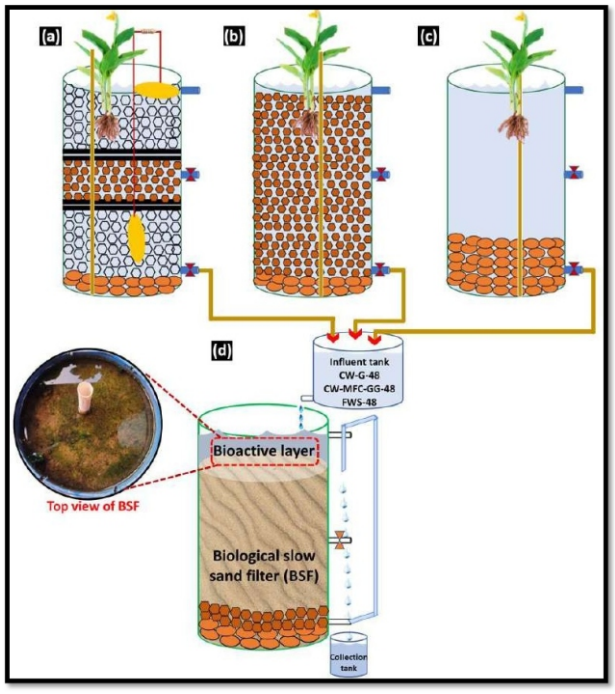


Figure: 1. Schematic view of (a) constructed wetland cum microbial fuel cell with granular graphite (CW-MFC-GG), (b) constructed wetland with garden gravel (CW- G), (c) free water surface (FWS), and (d) biological slow sand filter (BSSF) with enlarged view of its top bioactive layer.

Macrophytes growth assessment

After transplanting macrophytes into each microcosm, they exhibit robust root development and growth throughout the experimental period. As shown in Figure 2a, b, and c, root length increased from 14 cm to 37.75 cm and 34.57 cm for CW-G and CW-MFC-GG, respectively, at the conclusion of the investigation. The length of the CW-G and CW-MFC-GG shoots increased from 70 8 cm to 139.03 cm and 133.07 cm, respectively. The increased root and shoot length indicated that the macrophytes' growth conditions in the microcosms were optimal for reproduction. Due to the lack of substrates, macrophytes in the FWS microcosm were unable to proliferate. In addition to Typha angustifolia, Juncus gerardii, Iris pseudacorus, and Phragmites australis [24], a comparable

increase in root and shoot growth has been observed in CW and CW-MFC microcosms with various types of vegetation. After harvesting the macrophytes from the microcosms, CW-MFC-GG and CW-G had a total moist weight of 4.25 kg and 4.62 kg, respectively. The total dry biomass calculated for CW-MFC-GG was 48.89 kg m-2. In contrast, CW-G had a total dry biomass of 50,313 kg m-2. Due to the position of the HDPE liner (double plastic layer) in CW-MFC-GG, the total dry biomass of CW-MFC-GG may differ slightly from that of CW-G. It was placed just beneath the macrophytes to prevent root crossing into the CW-MFC-GG anodic region. This may have impeded root development, resulting in a moderate reduction in the total dry biomass of CW-MFC-GG relative to CW-G. In addition, the total working volume reduction in microcosms was calculated from the beginning of the experiment (planting a plant sapling) to the conclusion of the experiment (Canna indica plant growth with fully developed flowers). The greatest volume reduction was observed for CW-G at 16.41%, followed by CW-MFC-GG at 10.81% and FWS at 4.69%. One of the phenomena associated with volume reduction is the generation of sediment [24]. Long-term, the accumulation of organic and inorganic substances in sludge can result in system obstruction and a shortened lifespan. Clogging can further confound the removal of pollutants from the system and hinder the system's treatment performance [22]. CW-G exhibited the greatest volume reduction among substrate-based microcosms, i.e., CW-G and CW-MFC-GG; this indicates that CW-G will reach the congestion stage with diminished treatment performance earlier than CW- MFC-GG. Similar findings are reported by Srivastava et al. [19], who observed a volume reduction of 1.3 L in CW versus 0.5 L in CW-MFC. In addition, the lowest volume reduction in FWS was a result of its design and configuration, which lacked a substrate. The maximal volume reduction in CW-G corresponded with the total dry biomass production, i.e., was greatest in CW-G. This indicates that the root expansion of CW-G consumes more void spaces over time, resulting in the maximal volume reduction of the microcosm. In the case of CW- MFC-GG, disparities in disinfection efficiency, pollutant removal performance, and electricity production can also result from differences in root growth and biomass [16].



Figure: 2. (a) Initially planted Canna indica sapling, (b) and (c) harvested CW and CW- MFC microcosms Canna indica biomass after end of experiment, respectively.

CONCLUSION

In terms of total coliform, faecal coliform, E. coli, and turbidity removal, the present investigation demonstrated promising results with a combination of CW-MFC- GG followed by BSSF as secondary and tertiary wastewater treatment technologies, respectively. In contrast, the treatment efficacy of the CW-MFC-GG microcosm was marginally inferior to that of the CW-G microcosm due to the extremely low BOD/COD ratio of the complex wastewater. Nevertheless, the high volume reduction in CW-G indicates a high amount of sludge generation, which suggests early obstruction, unstable long-term performance, and a shortened lifespan over time. In spite of this, both CW-G-BSSF and CW-MFC-GG-BSSF have met the standard discharge limits for

COD and phosphate concentrations, and most importantly, the total coliform and faecal coliform numbers in the effluent pass the stringent regulations for reuse in agricultural applications, along with the absence of coliform E. coli. BSSF as tertiary treatment has played a significant role in obtaining disinfection via a biologically active schmutzdecke layer, whereas wastewater treatment was primarily achieved through secondary treatment technologies such as CW-G, CW- MFC-GG, and FWS. However, additional research will be required to optimize the systems in continuous mode and to evaluate the sustainability of the integrated process through life-cycle assessment studies.

REFERENCES

1. M. Hejazi, J. Edmonds, L. Clarke, P. Kyle, E. Davies, V. Chaturvedi, M. Wise,
   P. Patel, J. Eom, K. Calvin, Long-term global water projections using six socioeconomic scenarios in an integrated assessment modeling framework, Technol. Forecast. Soc. Change. 81 (2014) 205–226.
2. M. Narayan, P. Solanki, R.K. Srivastava, Treatment of sewage (domestic wastewater or municipal wastewater) and electricity production by integrating constructed wetland with microbial fuel cell, in: Sewage, IntechOpen, 2018.
3. World Health Organization, WHO guidelines for the safe use of wasterwater excreta and greywater, World Health Organization, 2006.
4. R. Iglesias, E. Ortega, G. Batanero, L. Quintas, Water reuse in Spain: data overview and costs estimation of suitable treatment trains, Desalination. 263 (2010) 1–10.
5. C. Corbella, M. Garfí, J. Puigagut, Long-term assessment of best cathode position to maximise microbial fuel cell performance in horizontal subsurface flow constructed wetlands, Sci. Total Environ. 563 (2016) 448–455.
6. L. Xu, Y. Zhao, C. Tang, L. Doherty, Influence of glass wool as separator on bioelectricity generation in a constructed wetland-microbial fuel cell, J. Environ. Manage. 207 (2018) 116–123.
7. Y. Yang, Y. Zhao, C. Tang, R. Liu, T. Chen, Dual role of macrophytes in constructed wetland-microbial fuel cells using pyrrhotite as cathode material: A comparative assessment, Chemosphere. 263 (2021) 128354.
8. R.P. Shingare, P.R. Thawale, K. Raghunathan, A. Mishra, S. Kumar, Constructed wetland for wastewater reuse: Role and efficiency in removing enteric pathogens, J. Environ. Manage. 246 (2019) 444–461.
9. R. Alufasi, J. Gere, E. Chakauya, P. Lebea, W. Parawira, W. Chingwaru, Mechanisms of pathogen removal by macrophytes in constructed wetlands, Environ. Technol. Rev. 6 (2017) 135–144.
10. R. Yang, M. Liu, Q. Yang, Microbial fuel cell affected the filler pollution accumulation of constructed wetland in the lab-scale and pilot-scale coupling reactors, Chem. Eng. J. 429 (2022) 132208.
11. F. Andreoli, L. Sabogal-Paz, Household slow sand filter to treat groundwater with microbiological risks in rural communities, Water Res. 186 (2020) 116352.
12. C.R. Bolton, D.G. Randall, Development of an integrated wetland microbial fuel cell and sand filtration system for greywater treatment, J. Environ. Chem. Eng. 7 (2019) 103249.
13. I. Kader Yettefti, F.E. Aboussabiq, S. Etahiri, D. Malamis, O. Assobhei, Slow sand filtration of effluent from an anaerobic denitrifying reactor for tertiary treatment: A comparable study, using three Moroccan sands, Carpathian J. Earth Environ. Sci. 8 (2013) 207–218.
14. T. Ahmed, S. Baidya, M. Acharjee, T. Rahman, Qualitative analysis of drinking water through the most probable number (MPN) method, Stamford J. Microbiol. 3 (2013) 9–16.
15. A. Torrens, P. Molle, C. Boutin, M. Salgot, Removal of bacterial and viral indicator in vertical flow constructed wetlands and intermittent sand filters, Desalination. 246 (2009) 169–178. https://doi.org/10.1016/j.desal.2008.03.050.
16. C. Ajonina, C. Buzie, R.H. Rubiandini, R. Otterpohl, Microbial pathogens in wastewater treatment plants (WWTP) in Hamburg, J. Toxicol. Environ. Health A. 78 (2015) 381–387.
17. A. Tiwari, S.I. Niemelä, A. Vepsäläinen, J. Rapala, S. Kalso, T. Pitkänen, Comparison of Colilert-18 with miniaturised most probable number method for monitoring of Escherichia coli in bathing water, J. Water Health. 14 (2016) 121– 131.
18. L. Du, X. Trinh, Q. Chen, C. Wang, H. Wang, X. Xia, Q. Zhou, D. Xu, Z. Wu, Enhancement of microbial nitrogen removal pathway by vegetation in Integrated Vertical-Flow Constructed Wetlands (IVCWs) for treating reclaimed water, Bioresour. Technol. 249 (2018) 644–651. https://doi.org/10.1016/j.biortech.2017.10.074.
19. P. Samantray, B.K. Mishra, C.R. Panda, S.P. Rout, Assessment of water quality index in Mahanadi and Atharabanki Rivers and Taldanda Canal in Paradip area, India, J. Hum. Ecol. 26 (2009) 153–161.

20. P. Srivastava, R. Abbassi, A. Yadav, V. Garaniya, M. Asadnia, T. Lewis, S.J. Khan, Influence of applied potential on treatment performance and clogging behaviour of hybrid constructed wetland-microbial electrochemical technologies, Chemosphere. 284 (2021) 131296. https://doi.org/10.1016/j.chemosphere.2021.131296.
21. C. Corbella, J. García, J. Puigagut, Microbial fuel cells for clogging assessment in constructed wetlands, Sci. Total Environ. 569–570 (2016) 1060–1063. https://doi.org/10.1016/j.scitotenv.2016.06.163.
22. V.K. Tyagi, A.A. Khan, A.A. Kazmi, I. Mehrotra, A.K. Chopra, Slow sand filtration of UASB reactor effluent: A promising post treatment technique, Desalination. 249 (2009) 571–576. https://doi.org/10.1016/j.desal.2008.12.049.
2z3. P. Ranjan, M. Prem, Schmutzdecke-a filtration layer of slow sand filter, Int. J. Curr. Microbiol. Appl. Sci. 7 (2018) 637–645.
24. Y. Takahashi, T. Nakashima, Actinomycetes, an inexhaustible source of naturally occurring antibiotics, Antibiotics. 7 (2018) 45.

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ANALYSIS OF BACTERIAL POPULATION IN DAIRY PRODUCTS USING THE STANDARD PLATE COUNT (SPC) METHOD

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ABSTRACT

Microbiological count methods are the standard laboratory techniques for estimating the microbial population of a sample. The dairy industry and regulatory enforcement agencies use these procedures to determine the quality of unprocessed and processed milk and to detect microbial contamination. This is achieved by testing producer, inline, and retail samples. Cultured dairy products (e.g., cultured buttermilk, fermented acidophilus, etc.), dairy products to which bacterial cultures have been added, and acidified products are typically not tested for total microbial decomposition content. Standard plate count (SPC) agar is the most commonly used method for microbiological counting. The dairy industry uses this method to estimate microbial populations in most types of dairy products and samples, as well as to determine quality and sources of contamination at successive processing stages. The SPC, which is the NCIMS-recognized reference method and specified in the Grade A Pasteurized Milk Ordinance,35 estimates the microbial population (primarily mesophilic, aerobic, and facultative bacteria) of raw and pasteurized milk and milk products.

KEY WORDS: Butter, Cheese, Yoghurt, Curd, Raw Milk, Standard Plate Count Method, Pasteurized Milk and Milk Products.

INTRODUCTION

India is an agricultural nation that has undergone the white revolution and developed diverse dairy products to satisfy the needs of a growing population. Indian nationals consume a substantial quantity of dairy products such as lussy, shrikhand, basundi, ice cream, badam shake, etc. as desserts. Since the beginning of human civilization, however, these foods have always been subject to preservation errors over the long term. Due to improper preservation and storage facilities in India in cold environmental settings (1, 2, 12), Indians are losing value-added food products, resulting in a loss for the manufacturer's economy and a worsening of malnutrition in the country, particularly in areas of poverty.

In this review, we focused on the most significant issues pertaining to the spoilage and preservation of milk and milk products, as well as the probable solutions that would support the economy and enhance the health of people, resulting in a superior economic status for producers (3).

MICROBIAL SPOILAGE

Microorganisms are the microscopic organisms responsible for the rapid deterioration of milk and milk products. Milk is lacteal secretion that is pure, fresh, and complete, and it is obtained from animals that are milked (4, 5). According to Sowmya Y, milk spoilage is the deterioration of its flavor, texture, and pigment that renders it unfit for human consumption. Milk is a potentially nutritive medium for the proliferation of microorganisms (6, 7, 8). Likewise, spoilage of milk and its derivatives may result in flavor and texture changes. Similarly, bitterness and moldiness can develop in milk products (9, 14). Important dairy products become inedible when decomposition alters their flavor, nutritional value, and texture (3). Mahendra Pal and Vijay J Jadhav proposed a similar viewpoint and reported that deterioration is responsible for altering the texture, flavor, and nutritive value of dairy products, thereby rendering them unsafe for human ingestion.

Globally, contamination of milk and its products by microorganisms is a significant problem. It occurs during the processing of dairy products like khoa (10). Khoa on the market was contaminated with microorganisms due to a delay between processing and selling, primary bioburden on used implements, and improper handling and storage procedures (11). Spoilage of food materials by microorganisms is caused by the degradation of fats, proteins, and carbohydrates by microorganisms or by enzymes produced by them (12).

There are numerous contamination sources for milk and milk products. The presence of feces can contaminate pera, burfi, and khoa (14). Numerous microflora are responsible for the degradation of milk and milk-based products. Pathogenic microflora, such as Salmonella typhi, E. coli, etc., can persist for extended periods in khoa, according to Bhat et al. Similarly, the presence of staphylococci and other food-spoiling organisms led to the loss of dairy products, exposing consumers to a substantial health risk (11). Milk with a higher water content is susceptible to microbial proliferation. Due to its high water and biochemical content, milk also serves as an optimal growth medium for numerous microbiota (12). In addition, it provides the essential nutrients required for microbial proliferation.

Additionally, inadequate sanitation practices contribute to the decomposition of milk. According to Khan A.Q., low-quality cleaning in the production unit leads to microbial contamination, which reduces the shelf life of final products, and many products are introduced to the market with negligent packaging and exposure to environmental contamination. Similarly, milk and milk products become contaminated during marketing due to improper storage and handling. Khoa and delicacies derived from it become contaminated even when processed in sterile environments, and in India, molds contaminate dairy foods due to humid conditions (13).

To promote high-quality products on the international market, it is recommended that milk and milk products undergo microbial evaluation. This view was supported by Agarwal and Rachappa (6), who argued that dairy products must be evaluated because they can become contaminated at any point from the farm to the consumer, including during storage, transportation, and packaging. Compared to organized areas, khoa samples collected from local level vendors had higher coliform counts (9), which are indicators of the presence of pathogens.

In addition, washing-related operations contribute to the deterioration of dairy products. Similarly, inferior cleaning and water used for utensil cleansing lead to bacterial contamination of khoa and khoa-based products. In accordance, the

authors concluded that the contamination in khoa-based sweets was caused by the bulk preparation of the product and its extended storage at room environmental conditions such as temperature. Mold, coliform, and yeast exceeded the Indian Standards Bureau 1479 limits in Khoa samples from private manufacturing facilities and local vendors in 1977. Milk decomposition is caused by an improper pasteurization process, adulteration in pasteurized milk, and unsanitary handling procedures. In addition, storage duration and location impact the quality of milk and milk products. In addition, microbial contamination may result from the use of khoa that has been stored for an extended period of time..

MATERIALS AND METHODS

In Meerut district, Uttar Pradesh, India, five distinct varieties of dairy products, including raw milk, curd, cheese, yogurt, and butter, were collected for this study. Raw milk was collected from Daurala, whey from Pallavpuram, cheese from Shastrinagar, yogurt from Sivaya, and butter from Begumpul.

ESTIMATION OF BACTERIAL POPULATION IN DAIRY PRODUCTS USING THE STANDARD PLATE COUNT (SPC) METHOD

Using the Standard plate count (SPC) method, the total bacterial population in collected dairy products (Raw milk, Cure, Cheese, Yoghurt, and Butter) was determined. The gathered dairy products were serially diluted up to a concentration of 10-6. One milliliter of samples were pipetted into a sterile petri dish containing Nutrient agar. They were thoroughly combined and permitted to solidify. There were three replications, and the uninoculated platters served as a control. After 24 hours of incubation at 281oC, the colonies of bacteria that appeared on the plates were enumerated using a Qubec colony counter and expressed as 10-4 cfu/ml.

EVALUATION OF THE TOTAL COLIFORM COUNT (TCC)

Using the Total coliform count (TCC) method, the coliform population in collected dairy products (Raw milk, Cure, Cheese, Yoghurt, and Butter) was determined. The gathered dairy products were serially diluted up to a concentration of 10-6. One ml of samples was pipetted onto a sterile petridish with Coliform agar. They were thoroughly combined and permitted to solidify. There were three replications, and the uninoculated platters served as a control. After 24 hours of incubation at 281oC, the coliform colonies that appeared on the plates were enumerated using a Qubec colony counter and expressed as 10-3 cfu/ml.

RESULTS AND DISCUSSION

DETAILS OF DAIRY PRODUCT SAMPLE COLLECTION LOCATION

In Meerut district, Uttar Pradesh, India, five distinct varieties of dairy products, including raw milk, curd, cheese, yogurt, and butter, were collected for this study. Raw milk was collected from Daurala, whey from Pallavpuram, cheese from Shastrinagar, yogurt from Sivaya, and butter from Begumpul.

Tabulated in Table – 1 are the locations where samples of dairy products were taken.

Table – 1: Details of location of Dairy product sample collection

Name of the District	Name of the location	Dairy samples
Meerut District, Uttar Pradesh, India.	Daurala	Raw milk
	Pallavpuram	Curd
	Shastrinagar	Cheese
	Sivaya	Yoghurt
	Begumpul	Butter

ESTIMATION OF BACTERIAL POPULATION IN DAIRY PRODUCT SAMPLES BY STANDARD PLATE COUNT (SPC) TECHNIQUE

The bacterial population in five collected samples of dairy products, namely Raw milk, Curd, Cheese, Yoghurt, and Butter, was estimated using the Standard plate count technique (SPC), and the results are presented in Table – 2. Curd sample had the highest bacterial population among the five milk products with 9.4 104 cfu/ml, followed by Cheese (8.6 104 cfu/ml), Raw milk (7.1 104 cfu/ml), and Yoghurt (6.5 104 cfu/ml). Butter had the smallest population (5.3 104 cfu/ml). Begumpul samples contained the greatest number of microbes, followed by those from different location as the lowest population density.

Table – 2: Estimation of bacterial population by Standard Plate Count (SPC) technique

S. No	Milk products	Bacterial population estimated by Standard Plate Count (SPC) technique (×104 cfu/ml)				
		Chidam baram	Annam alai Nagar	Bhuvan agiri	Sethiyat hope	Cuddal ore
1	Raw milk	5.4	6.3	4.6	5.2	7.1
2	Curd	7.2	8.5	6.3	6.9	9.4
3	Cheese	6.5	7.8	5.5	6.2	8.6
4	Yoghurt	4.2	5.9	3.8	4.7	6.5
5	Butter	3.6	4.1	2.4	3.5	5.3
S.Ed		0.67	0.76	0.67	0.59	0.73
CD (P = 0.05)		1.35	1.54	1.34	1.19	1.47

ESTIMATED TOTAL COLIFORM NUMBER (TCC)

The total coliform count of the collected dairy product samples (Raw milk, Curd, Cheese, Yogurt, and Butter) was calculated, and the results are presented in Table – 3. Curd had the highest coliform count among milk products at 5,4 103 cfu/ml, followed by Raw milk at 4,3 103 cfu/ml. Cheese had the lowest coliform count (3.2 103 cfu/ml). There were no coliforms found in the Yogurt and Butter samples. Maximum coliform count was observed in the samples collected from Begumpul followed by Pallavpuram, Daurala and Sivaya. Shastrinagar's coliform population was found to be the lowest.

Table – 3: Estimation of Total Coliform Count (TCC)

S. No	Milk products	Total Coliform Count (TCC) (×103 cfu/ml)				
		Chidam baram	Annam alai Nagar	Bhuvan agiri	Sethiyat hope	Cuddal ore
1	Raw milk	2.3	3.7	1.6	2.8	4.3
2	Curd	3.3	4.8	2.6	3.5	5.4
3	Cheese	1.4	2.6	0.7	1.9	3.2
4	Yoghurt	-	-	-	-	-
5	Butter	-	-	-	-	-
S.Ed		0.54	0.63	0.54	0.46	0.63
CD (P = 0.05)		1.29	1.26	1.08	0.92	1.26

CONCLUSION

Microbiological count methods are the standard laboratory techniques for estimating the microbial population of a sample. The dairy industry and regulatory enforcement agencies use these procedures to determine the quality of unprocessed and processed milk and to detect microbial contamination. This is achieved by testing producer, inline, and retail samples. Cultured dairy products (e.g., cultured buttermilk, fermented acidophilus, etc.), dairy products to which bacterial cultures have been added, and acidified products are typically not tested for total microbial decomposition content. Standard plate count (SPC) agar is the most commonly used method for microbiological counting. The dairy industry uses this method to estimate microbial populations in most types of dairy products and samples, as well as to determine quality and sources of contamination at successive processing stages. The SPC, which is the NCIMS-recognized reference method and specified in the Grade A Pasteurized Milk Ordinance,35 estimates the microbial population (primarily mesophilic, aerobic, and

facultative bacteria) of raw and pasteurized milk and milk products.

Milk and milk products that spoil pose a significant health risk because they cause disease outbreaks. Current preservation methods for milk and milk products, such as pasteurization, are inadequate because they do not guarantee the microbiological safety of milk and milk products. Therefore, it is necessary to devise techniques and methods of the next generation for their preservation. In addition, standard training of individuals, quality cleaning practices, recommended preservation and transportation facilities, etc., may aid in meeting the global demand for milk and milk products for an extended period of time by increasing their stabilities.

REFERENCES

1. Dosti B. Z., Guzel-Seydim and Greene A. K. 2005. Effectiveness of ozone, heat and chlorine for destroying common food spoilage bacteria in synthetic media and biofilms. International Journal of Dairy Technology, 58: 19-24.
2. De, S. 2001. Outlines of Dairy Technology. Oxford University Press. New Delhi, India.
3. Sandrou, D. K. and Arvanitoyannis I. S. 2000. Application of Hazard Analysis Critical Control Point (HACCP) system to the cheese- making industry: A review. Food Reviews International, vol. 16, no. 3, pp. 327–368.
4. Eckner, F. K. and Zottola, E. A. 1991. Potential for the low-temperature pasteurization of dairy fluids using membrane processing. Journal of Food Protection, 54: 793-797.
5. Elwell M. W. and D. M. Barbano 2006. Use of microfiltration to improve fluid milk quality. Journal of Dairy Science, 89: E10- E30.
6. Eneroth, A., Christiansson, A., Brendehaug J. and Molin G. 1998. Critical contamination sites in the production line of pasteurized milk, with reference to the psychrotrophic spoilage flora. International Dairy Journal, 8: 829-834.
7. Fromm, H. I. and Boor, K. J. 2004. Characterization of pasteurized fluid milk shelf-life attributes. Journal of Food Science, 69: M207- M214.
8. Ghodekar, D. R., Ranganathan B. and Dudani, A. T. 1980. Yeast and moulds in indigenous milk products. Indian Journal of Dairy Science, 33: 255-259.
9. Melisa Anderson, Patrice Hinds, Stacyann Hurditt, Princena Miller, Donovan McGrowder and Ruby Alexander-Lindo 2011. The microbial content of unexpired pasteurized milk from selected supermarkets in a developing country. Asian Pacific Journal of Tropical Biomedicine, 1(3): 205–211.
10. Nada, S., D. Ilija, T. Igor, M. Jelena and G. Ruzica 2012. Implication of food safety measures on microbiological quality of raw and pasteurized milk. Food Control, 25: 728-731.
11. Sharma, G. R. K. 2016. Effectiveness of multimedia modules on dissemination of knowledge among the dairy farmers. Journal of Research and Development, 4:1-3.
12. Santana, E. H. W., Beloti, V., Gusmao, V. V. 2004. Milk contamination in different points of dairy process. Seminar, Cynic's Vagaries, Londrina 25: 349-358.
13. S. Sarkar 2015. Microbiological Considerations: Pasteurized Milk. International Journal of Dairy Science, 10:206-218. Sarkar, S. 2016. Microbiological Safety Concerns of Raw Milk. Journal of Food, Nutrition and Dietetics, 1 (2): 105.
14. Sheela Mary, M. and Shrinithivihahshini, N. D. 2017. Pervasiveness of Listeria monocytogenes in Milk and Dairy Products. Journal of Food Microbiology, safety & hygiene, Vol 2(3):125.

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EFFECT OF GIBBERELLIC ACID AND BORON ALONE AND ITS COMBINATION ON VEGETATIVE GROWTH, FRUITING AND YIELD OF PHALSA

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ABSTRACT

An experiment was conducted to study the effect of gibberellic acid and boron alone and in combination on vegetative growth, fruiting and yield of phalsa in Garden, Department of Fruit Science, Chandra Shekhar Azad University of Agriculture and Technology Kanpur, Uttar Pradesh in the year 2022-23 using nine treatments *viz.*, T_1-Control-water spray, T_2-0.3% boron, T_3-0.6% boron, T_4-30ppm GA_3, T_5-40ppm GA_3, T_6-30ppm GA_3+ 0.3% boron, T_7-40ppm GA_3+ 0.3% boron, T_8-30ppm GA_3+ 0.6% boron and T_9-40ppm GA_3+ 0.6% boron, which were replicated thrice in randomized block design. The results of the experiment revealed that the foliar application of gibberellic acid and boron either alone or in combination is more effective as compared to control. Among all treatments, pre-harvest application of 40ppm of GA_3 + 0.6% of boron produced maximum shoot length (142.69cm), diameter of shoot (0.98cm), number of shoots per plant (94.68), number of leaves per shoot (45.86), number of fruits per shoot (83.46), fruit set (76.02%), yield per plant (6.48kg), yield per hectare (99.73q), fruit diameter (1.08cm), weight of 100 fruit (101.68g), and fruit volume (1.30cc) followed by 30ppm of GA_3 + 0.3% of boron as compared to rest of other treatments including control. As the chemical quality parameters are concerned the fruits having maximum total soluble solids (26.41°Brix), total sugars (20.06%), reducing sugar (16.08%), non-reducing sugar (3.98%), ascorbic acid (41.68mg) and reduced titratable acidity (2.32%) were recorded in fruits from produced from the plants treated with 40ppm of GA_3 + 0.6% of boron in the plains of northern India.

Keywords: Phalsa, GA3, Boron, Growth, Fruiting, Yield and Quality

INTRODUCTION

Phalsa (*Grewia subinaequalis* DC), which is also known as Indian Sherbet berry, belongs to the family Tiliaceae, is mainly grown for its delicious fruits. Fruits are rich in carbohydrates, fibers, proteins, vitamins A, B, C, and various minerals like potassium, calcium, iron and phosphorus. The phytochemicals present in phalsa fruit include anthocyanins, tannins, phenols and flavonoids **(Mehmood *et al.*, 2020).**

Application of growth substances *viz.,* auxins and gibberellins have an effective role in increasing fruit set, yield and quality in several fruits including phalsa. Role of micronutrients also can not be neglected, although they are needed in minor quantities as they play an important role in plant metabolism which cannot be replaced by other

elements. Micronutrient deficiency induces several physiological disorders, which compromise plant growth and subsequently reduce fruit quantity and quality. Boron is also essential for a wide variety of plant processes, including the creation and stability of cell walls and the preservation of the structural and functional integrity of biological membranes. Boron starts the flow of sugar or energy into plant growth, pollination and seed germination. The production of excellent fruits in phalsa crops, protein synthesis and creation of vascular bundles, root system, fruit development, and seed germination are all maintained by boron level.

Use of gibberellic acid also promotes elongation, development and expansion of cells, which results in an increased fruit size. Application of gibberellic acid during specific growth stages, such as fruit developmental state, can potentially enhance the size of fruits.

Keeping the above facts in view, the present investigation was planned to assess the effect of different concentrations of gibberellic acid and boron alone and its combination on vegetative growth, fruiting and yield of phalsa in the plains of northern India.

MATERIAL AND METHODS

The experiment was conducted on the thirty-year-old, uniform in growth phalsa cv. Sharbati plants, spaced at 2 x 2 m apart in the Garden, Department of Fruit Science, Chandra Shekhar Azad University of Agriculture and Technology, Kanpur (U.P.) during the year 2022-23. The experiment was laid out using nine treatments *viz.,* T_1-Control-water spray, T_2-0.3% Boron, T_3-0.6% Boron, T_4-30ppm GA_3, T_5-40ppm GA_3, T_6-30ppm GA_3+ 0.3% Boron, T_7-40ppm GA_3+ 0.3% Boron, T_8-30ppm GA_3+ 0.6% Boron and T_9-40ppm GA_3+ 0.6% Boron, which were replicated thrice in randomized block design. The crop received its initial foliar spray of micro-nutrients and plant growth regulators when the buds were fully swollen in the second week of March on randomly tagged plants and the second spraying was done at the pea stage of fruit in the first week of April.

During experimentation period observations were recorded on vegetative growth parameters using standard techniques. Weight of 100 fruits and yield per plant were recorded during each picking using weighing machine. Ten randomly chosen fruits were measured using a vernier caliper for their diameter and expressed in centimeters (cm). Volume of fruits were determined by water displacement method, and expressed in cc. The total soluble solids content of fruits was measured using Earma hand refractometer. The procedures described in **A.O.A.C. (1980)** were used to determine total sugars, titratable acidity and ascorbic acid contents in phalsa fruits.

RESULT AND DISCUSSION

Shoot length (cm)

It is obvious from Table 1 that foliar spray of GA_3 and boron proved significantly effective in improving the length of shoots. The maximum shoot length (142.69 cm) was recorded under the treatment of 40 ppm GA_3 + 0.6% boron, followed by the application of 30 ppm GA_3 + 0.3% boron (137.85cm), whereas, untreated plants resulted in minimum shoot length (112.36cm). This increase in vegetative growth of the phalsa plant with the spray of plant growth regulator and micronutrient combination at a higher rate may be due to the association of nitrogen in the synthesis of protoplasm and the primary manufacture of amino acids with increased auxin activities. As a result, meristematic activities increased which enhanced the vegetative growth. Similar results have also been reported by **Karole and Tiwari (2016)** with spray of NAA + GA_3 + urea in ber and **Kumar *et al.*, (2014)** in phalsa.

Diameter of shoot (cm)

The data presented in Table 1 also showed a significant difference in the diameter of phalsa shoots. The maximum diameter of shoot (0.98cm) was recorded in plants which were treated with the combination of 40ppm of GA_3 + 0.6% of boron, followed by the application of 30ppm GA_3 + 0.3% boron (0.95cm). However, the untreated plants produce the minimum diameter of shoot (0.68cm). The effect of foliar nutrition of boron, GA_3 and their combined treatments promoted the diameter of phalsa shoots positively and consistently during the investigation period. An increase in doses of boron and levels of GA_3 concentration results in an increase in the diameter of shoots of phalsa. The above results are in agreement with the findings of **Jitendra *et al.*, (2017)** in phalsa and **Shukla *et al.*, (2009)** in aonla, who also recorded maximum diameter of shoots with GA_3 and boron application.

Number of shoots per plant

Plants sprayed with the combination of 40ppm GA_3 + 0.6% boron (T_9) produced the maximum number of shoots per plant (94.68), closely followed by the application of 30ppm GA_3 + 0.3% boron (92.41), while plants sprayed only with water (T_1-control) produced minimum number of shoots (75.31) per plant (Table 1). This increase in number of shoots might be due to the fact that gibberellin given in the form of GA_3 sprayed is a constituent of protein which is essential for the formation of protoplasm and thus, affects cell division and cell elongation. All these factors contributed to cell multiplication, which has resulted in better photosynthetic activity and its translocation to promote better vegetative growth. Thus, increased number of leaves per shoot with the spray of GA_3. The findings are in agreement with the result of **Kumar *et al.*, (2014)** in phalsa.

Number of leaves per shoot

Number of leaves per shoot shows a significant increase in all sprayed plants as compared to the control. Maximum number of leaves (45.86) was recorded with the application of 40ppm GA_3 + 0.6% boron, followed by the application of 30ppm GA_3 + 0.3% of boron (43.76). The plants kept under control *i.e.,* without any application, produced minimum number of leaves (19.61) per shoot (Table 1). The favorable effect of GA_3 and boron in promoting number of leaves might be due to the abundant supply of GA_3 and boron on plant growth. Moreover, the increase in vegetative growth may also be attributed to an increased uptake of these elements which are a constituent of protein component of protoplasm, favorably influencing chlorophyll content in leaves. All these factors contributed to cell multiplication, which has resulted in better photosynthetic activity and its translocation to promote better vegetative growth. Thus increased number of leaves per shoot with the spray of gibberellic acid takes place. The findings are in agreement with the result of **Kumar *et al.*, (2014) in phalsa**

Number of fruits per shoot

The data presented in Table 1, showed a significant increase in number of fruits per shoot. The plants sprayed with the combination of 40 ppm GA_3 + 0.6% boron produced a maximum number of fruits per shoot (83.46), followed by 30 ppm GA_3 + 0.3% boron (78.63). The plants kept under control (T_1) produced minimum number of fruits per shoot (58.16). The application of gibberellic acid and boron can positively influence the number of fruits per shoot in phalsa. GA_3 promotes flowering, fruit set, and parthenocarpy, while boron ensures optimal pollen viability, fruit growth, and reproductive organ function. The synergistic interaction between gibberellic acid and boron enhances

pollination, fruit enlargement, and overall fruit production in phalsa plants. These results are similar to the finding of **Singh *et al.*, (2017) in phalsa and Singh *et al.*, (2023) in mango.**

Fruit set (%)

The data for fruit set per cent presented in Table 1 revealed that the application of GA_3 @ 40 ppm + boron @ 0.6% resulted in maximum fruit set percentage (76.02%) followed by the application of GA_3 @ 30 ppm + boron @ 0.3% (75.78%). However, the lowest fruit set was noticed in plants kept as untreated control (64.13%). GA_3 and boron can potentially enhance fruit set in phalsa through their effects on pollen germination, cell division and expansion, parthenocarpy induction, sugar transport, and cell wall formation. **Yadav *et al.*, (2020), Zeeshan and Singh (2018) in phalsa, Prasad *et al.*, (2005) in guava, and Singh *et al.*, (2001)** in ber also gave similar results in their findings.

Yield per plant (kg) and hectare (q/ha)

The data presented in Table 1, showed that the foliar sprays of gibberellic acid and boron proved significantly effective in improving the yield of phalsa per plant and hectare. The maximum yield per plant (6.48 kg) and per hectare (99.73q) were obtained with the application of 40ppm of GA_3 + 0.6% of boron, followed by the application of 30ppm GA_3 + 0.3% Boron (6.12kg and 94.93q, respectively), while lowest yield (3.41 kg and 58.80 kg, respectively) was recorded in plants kept under control. This increase in yield may be due to the reason that GA_3 promotes flowering, fruit set, and fruit size, while boron ensures proper pollination, fruit development, and nutrient utilization, which contributes to higher fruit production and improved overall crop performance. These results are similar to that of the findings reported by **Singh *et al.*, (2017), Yadav *et al.*, (2020) in phalsa and Vani *et al.*, (2021) in guava.**

Fruit diameter (cm)

The maximum fruit diameter (1.08 cm) was obtained with the application of 40 ppm GA_3 + 0.6% boron, followed by the application of 30ppm GA_3 + 0.3% boron (1.06cm), whereas, fruits with minimum diameter (0.93cm) were produced from the plants kept as untreated (Fig 1). The application of GA_3 and boron has a positive influence on the fruit diameter in phalsa. Use of gibberellic acid stimulates cell elongation, while boron supports cell division and overall fruit development. Their combined effects can result in larger and healthier fruits. Similar findings have been reported by different researchers such as **Singh *et al.*, (2023) in mango, Yadav *et al.*, (2020) and Zeeshan and Singh (2018) in phalsa.**

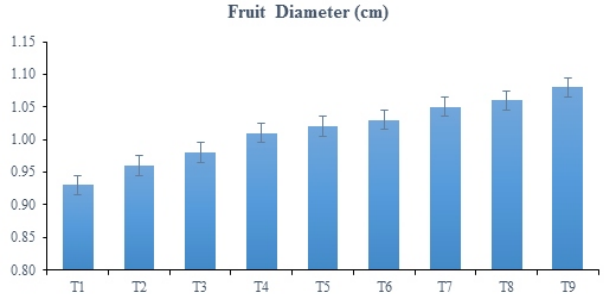


Fig. 1. Effect of foliar application of GA3 and boron on fruit diameter of phalsa fruits

Weight of 100 fruits (g)

The foliar sprays of GA_3 and boron proved significantly more effective in improving the weight of 100 fruits (Fig. 2). In this regard, the maximum weight of 100 fruits (101.68g) was obtained with the treatment of 40ppm GA_3 + 0.6% boron, followed by the treatment of 30ppm GA_3 + 0.3% boron (101.05g). However, minimum weight of 100 fruits (66.01g) was recorded which were produced from the plants kept under control (T_1). Similar results were also obtained by **Kaur *et al.*, (2017) in litchi, Vani *et al.*, (2021) in guava and Kumar *et al.*, (2023) in phalsa.**

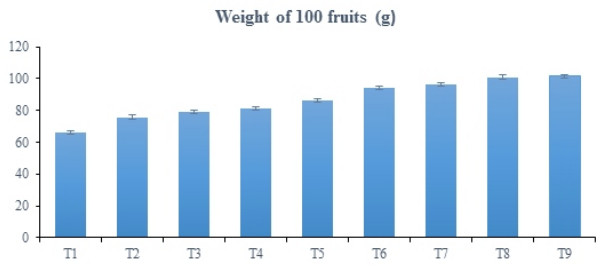


Fig. 2. Effect of foliar application of GA3 and boron on Weight of 100 fruits (g) of phalsa

Volume of fruit (cc)

Pre-harvest spray of plant growth regulator and micronutrient significantly altered the volume of phalsa fruits in comparison to plants which were sprayed only with normal water as control (Table 1). The maximum volume of fruit (1.30cc) was obtained with the treatment of 40 ppm GA_3 + 0.6% boron, followed by of 30 ppm GA_3 + 0.3% boron (1.29cc), while untreated fruit plants produced fruits having lowest volume (1.15cc). This increase in volume of fruits might be due to better supply of nutrients and photosynthates in plants treated with foliar application of GA_3 and boron might have made rapid synthesis of metabolites particularly carbohydrate and their translocation to the fruits causing relatively greater pulp content. The results are also in conformity with the findings of **Singh *et al.*, (2016) in guava, Shukla *et al*., (2009) in aonla, Dubey *et al.*, (2017) in strawberry, and Bhadauria *et al*., (2018) in aonla.**

Total Soluble Solids (°Brix)

Maximum accumulation of total soluble solids (26.41°Brix) content in phalsa fruit was recorded with the application of GA_3 40ppm + boron 0.6% followed by the treatment of GA_3 30ppm + boron 0.3% (25.82°Brix), while the minimum total soluble solids (17.10°Brix) was recorded in fruits which were produced from the plants kept under control (Table 2). This increase in total soluble solids content of fruits may be due to the facts that plant bio-regulator and micronutrient play an important role in photosynthesis which ultimately lead to the accumulation of carbohydrates and ultimately increase in total soluble solids content of fruits. The results of experiments are in accordance with the reports of **Singh *et al.*, (2023) in mango, Zeeshan and Singh (2018), Kumar *et al.*, (2023) in phalsa and Badal and Tripathi (2021),** who also found increased total soluble solids content in guava.

Sugars and Titratable acidity (%)

The significantly higher level of total sugars, reducing sugar and non-reducing sugar content (20.06%, 16.08% and 3.98%, respectively) were recorded in fruits which were produced from the plants treated with GA_3 40ppm + boron 0.6%, followed by treatment of GA_3 30ppm + boron 0.3% (19.56%, 15.72% and 3.84%, respectively), while the minimum value was recorded in fruits produced from plants kept under control (14.06%, 11.86% and 2.20%, respectively) without any application (Table 2). GA_3 indirectly influences many enzyme systems in plants, out of these the role of gibberellins in the activation of amylase enzyme is well known which are responsible for the conversion of starch into sugar thus improving the total sugars contents in fruits. These findings are in line with the reports of **Singh *et al.*, (2023) in mango, Kumar and Tripathi (2009) in strawberry, Kumar *et al.*, (2023)** for reducing and non-reducing sugar in phalsa. **Tripathi *et al.*, (2019)** also reported increased TSS and total sugars content in mango.

The minimum titratable acidity content in fruits (2.32%) was noted with the treatment of GA_3 40ppm + boron 0.6%, followed by treatment of GA_3 30ppm + boron 0.3% (2.37%), whereas, the maximum titratable acidity content was recorded in fruits produced in control (2.83%). This decrease in acidity content of fruits might be due to an increase in

total soluble solids and total sugars. The acids under the influence of chemicals might have either been converted into sugars and their derivatives by the reactions involving reversal of glycolytic pathway or may be used as a substratum in the respiration or both. These findings are in line with the reports of **Zeeshan and Singh (2018)** in phalsa, **Tripathi *et al.*, (2019)** in mango and **Kumar *et al.*, (2023)** in phalsa.

Ascorbic Acid

Significantly higher amount of ascorbic acid (41.68mg/100g) was found in fruits produced from the plant treated with GA_3 40ppm+ boron 0.6%, followed by the treatment of GA_3 30ppm + boron 0.3% (40.88 mg/100g), whereas, the minimum amount of ascorbic acid (28.30mg/100g) was recorded in fruits produced from the plants kept as control (Table 2). This increase in ascorbic acid content with gibberellic acid combination might be due to uninterrupted synthesis of its precursor like glucose-6-phosphate during the conversion of starch into various sugars and low rate of oxidation. The present findings are in accordance with the results of **Kaur *et al.*, (2017)** in litchi, **Tripathi *et al.*, (2019)** in mango and **Kumar *et al.*, (2023), Zeeshan and Singh (2018)** in phalsa.

Table 1: Effect of foliar application of GA3 and boron on vegetative growth, fruit set and physical parameter of phalsa

Treatments	Shoot Length (cm)	Diameter of shoot (cm)	No. of Shoots/plant	No. of leaves per shoot	No. of fruits/shoot	Fruit set (%)	Yield per plant (kg/plant)	Yield per hectare (q/ha)	Volume of fruit (cc)
T_1-Control-water spray	112.36	0.68	75.31	19.61	58.16	64.13	3.41	58.8	1.15
T_2-0.3% Boron	115.75	0.75	81.46	28.31	62.24	67.12	4.12	68.27	1.18
T_3-0.6% Boron	118.16	0.78	84.83	30.12	64.67	67.89	4.48	73.07	1.19
T_4-30ppm GA_3	122.61	0.81	86.34	35.61	66.40	69.32	4.96	79.47	1.21
T_5-40ppm GA_3	124.32	0.83	88.73	37.35	69.55	71.68	5.04	80.53	1.22
T_6-30ppm GA_3 + 0.3% Boron	129.21	0.88	90.31	39.14	72.16	74.06	5.46	86.13	1.25
T_7-40ppm GA_3 + 0.3% Boron	134.61	0.91	91.68	40.26	75.32	74.98	5.95	92.67	1.27
T_8-30ppm GA_3 + 0.6% Boron	137.85	0.95	92.41	43.76	78.63	75.78	6.12	94.93	1.29
T_9-40ppm GA_3 + 0.6% Boron	142.69	0.98	94.68	45.86	83.46	76.02	6.48	99.73	1.30
S.E.(m)+	**1.88**	**0.01**	**1.44**	0.60	**1.15**	**1.41**	**0.06**	**1.30**	**0.01**
C.D. at 5%	**5.70**	0.04	4.36	1.83	**3.48**	**4.28**	0.19	**3.93**	**0.05**

Table 2: Effect of foliar application of GA3 and boron on chemical quality parameter of phalsa

Treatments	T.S.S. (° Brix)	Total Sugar (%)	Reducing Sugar (%)	Non-reducing Sugar (%)	Titratable Acidity (%)	Ascorbic Acid (mg/100g)
T_1-Control-water spray	17.10	14.06	11.86	2.20	2.83	28.30
T_2-0.3% Boron	18.30	16.19	13.32	2.87	2.65	31.71
T_3-0.6% Boron	18.96	16.59	13.61	2.98	2.60	32.21
T_4-30ppm GA_3	20.06	17.26	14.04	3.22	2.58	34.48
T_5-40ppm GA_3	20.98	17.60	14.18	3.42	2.51	36.34
T_6-30ppm GA_3 + 0.3% Boron	22.68	18.16	14.48	3.68	2.45	37.98
T_7-40ppm GA_3 + 0.3% Boron	23.31	18.92	15.21	3.71	2.41	38.68
T_8-30ppm GA_3 + 0.6% Boron	25.82	19.56	15.72	3.84	2.37	40.88
T_9-40ppm GA_3 + 0.6% Boron	26.41	20.06	16.08	3.98	2.32	41.68
S.E.(m)+	**0.17**	**0.25**	**0.22**	0.05	0.04	0.49
C.D. at 5%	**0.53**	0.75	0.67	**0.17**	0.13	**1.49**

CONCLUSION:

Based on the findings of this study, it is concluded that foliar spray of borax and GA_3 on phalsa plants resulted in significant improvement in flowering, fruiting and yield characteristics, which ultimately also leads in the enhancement of physical and chemical attributets in phalsa. The higher concentration of gibberellic acid (40 ppm) with boron (0.6%) is more effective than their lower doses in increasing growth, flowering fruiting, yield and quality as compared to remaining all other treatments in the plains of North India.

REFERENCES:

1. **A.O.A.C. (1980).** Official method of analysis. Association of Official Analytical Chemists (12th edn.), Washington. D.C.
2. **Badal, D.S. and Tripathi, V.K. (2021).** Effect of foliar application of NAA and Boron on physio-chemical parameters of winter season guava (Psidium guajava L.) cv. Lucknow-49. *The Pharma Innovation Journal*, **10**(9): 928932
3. **Bhadauria, A. S., Tripathi, V.K., Singh, A. and Gupta, S. (2018).** Effect of foliar application of plant bio-regulators and micronutrients on fruit retention, yield and quality attributes of aonla. *Progressive Research-An International Journal*, **13**(3): 216-219.
4. **Dubey, V., Meena, M. L. and Tripathi, V. K. (2017).** Effect of plant bioregulators and micronutrient on vegetative growth, yield and quality of strawberry cv. Chandler. *Progressive Research-An International Journal*, **12** (3): 330-332.
5. **Jitendra, S. S.; Kasera, S.; Lal, D.; and Singh, V. K. (2017).** Effect of foliar spray of micro nutrients on plant growth, yield and fruit quality of phalsa (*Grewia asiatica* L.). *Environment & Ecology*, **35**(4A): 2841-2845.
6. **Karole, B. And Tiwari, R. (2016**) Effect of pre-harvest spray of growth regulators and urea on growth, yield and quality of ber under malwa plateau conditions, *Annals of Plant and Soil Research,* **18**(1):18-22.
7. **Kaur, S. (2017).** Effect of micronutrients and plant growth regulators on fruit set, fruit retention, yield and quality attributes in litchi cultivar Dehradun. Chemical *Science Review and Letters*, **6**(22):982-986.
8. **Kumar, R. and Tripathi, V. K. (2009).** Influence of NAA, GA_3 and Boric Acid on growth, yield and quality of strawberry cv. Chandler. *Progressive Horticulture,* **41**(1): 113-115.
9. **Kumar, D., Dwivedi, A. K., Tripathi, V. K. and Pandey, S. (2023).** Effect of NAA and GA_3 on growth, yield and quality attributes of phalsa (*Grewia subinaequalis* DC) cv. Sharbati. *Progressive Agriculture*, ***23***(1), 159-165.
10. **Kumar M., Dwivedi R., Kumar A. and Kumar A. (2014).** Effect of nutrient on physico-chemical characteristics of phalsa (*Grewia subinaequalis* D.C.) fruits. *Global Journal of Bio-Science and Biotechnology*, **3**(3): 320-323.
11. **Mehmood, A., Ishaq, M., Usman, M., Zhao, L., Ullah, A. and Wang, C. (2020).** Nutraceutical perspectives and value addition of phalsa (*Grewia asiatica* L.): A review. *Journal of Food Biochemistry*, ***44***(7):1-16.
12. **Prasad, B., Das, S., Chatterjee, D. and Singh, U.P. (2005).** Effect of foliar application of urea, zinc and boron on quality of guava. *Journal of Applied Bioscience*, **15**(1): 48-50.
13. **Shukla, H.S., Kumar, V. and Tripathi, V. K. (2009).** Effect of gibberellic acid and boron on development and quality of aonla fruits Banarasi. *Acta Horticulturae,* **890**:375-380.
14. **Singh, J., Pratap, B., Sohi, H. S. and Kumar, A. (2016).** Effect of zinc sulphate and gibberellic acid on physical characters and yield attributes of guava (*Psidium guajava* L.). *Res. Environ. Life Sci.,* **9**(3):340-342.
15. **Singh, R., Godara, N.R., Rajbir, S. and Dahiya, S. S. (2001).** Response of foliar application of growth regulators and nutrients in ber (*Ziziphus mauritiana* Lamk.) cv. Umran. *Haryana J. Hort. Sci.,* **30**(3&4): 161-164.
16. **Singh, B., Yadav, A. L. and Meena, A. K. (2017).**The Effect of Foliar Feeding of Plant Growth Regulators on Growth and Fruiting Behavior of Phalsa. *International Journal of Agriculture Innovations and Research,* **5**(5):806-808.
17. ***Singh, S. S., Tripathi, V. K. and Awasthi, M.* (2023).** Influence of Pre-harvest Application of Gibberellic Acid and Borax on Fruit Retention, Yield and Quality of Mango (*Mangifera indica* L.*)* cv. Dashehari. *Biological Forum-An International Journal,* **15**(9): 287-291.
18. **Tripathi, V. K., Singh, A., Bhadauria, A. S. and Gupta, S. (2019).** Influence of GA_3 and napthalene acetic acid alone and in combination on fruit drop, yield and quality of mango cv. Amrapali. *Progressive Research-An International Journal, 14(1):10-13.*
19. **Vani, N. U., Bhagwan, A., Kumar, A. K., Sreedhar, M., Sharath, S.R. and Suman, B. (2021).** Studies on effect of pre harvest sprays of plant growth regulators and micronutrients on yield and economics of guava (*Psidium guajava* L.) cv. Lucknow-49. *Journal of Pharmacognosy and Phytochemistry,* **10**(1), 413-418.
20. **Zeeshan, M. and Singh, J. P. (2018).** Studies on foliar application of boron and GA_3 on physico-chemical composition and yield of phalsa (*Grewia subinaequalis* DC). *HortFlora Research Spectrum*, **7**(1), 52-57.
21. **Yadav, A. K., Singh, J.P., Choudhri, H. P. S. and Singh, V. (2020).** Effects of foliar application of boron and Gibberellic acid on growth and fruit set of phalsa (Grewia asiatica L.). *Journal of Pharmacognosy and Phytochemistry,* **9**(2): 700-703.

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INFLUENCE OF DIFFERENT LEVELS OF BORON AND NAA ON FRUITING, YIELD AND QUALITY ATTRIBUTES OF LITCHI (LITCHI CHINENSIS SONN.)

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ABSTRACT

An experiment was carried out in the Garden, Department of Fruit Science, C.S. Azad University of Agriculture and Technology, Kanpur (U.P.) Indiaduring January to June 2023 to study the effect of different levels of boron and NAA on fruiting, yield and quality of litchi using sixteen treatments *viz.*,T_1 (20 ppm NAA),T_2 (30ppm NAA), T_3 (40ppm NAA), T_4 (0.2% boron), T_5 (0.2% boron + 20ppm NAA), T_6 (0.2% boron + 30ppm NAA), T_7 (0.2% boron + 40ppm NAA),T_8 (0.2% boron), T_9 (0.4% Boron+20ppm NAA), T_{10} (0.4% boron+ 30ppm NAA), T_{11} (0.4% boron+ 40ppm NAA), T_{12} (0.6% boron), T_{13} (0.6% boron+ 20ppm NAA), T_{14} (0.6% boron + 30ppm NAA), T_{15} (0.6% boron+ 40ppm NAA) and T_{16} (control water spray), replicated thrice in Factorial Completely Randomized Design. Uniform and healthy plants of litchi cv. Dehradun was selected and each plant with similar three branches was identified and that was used as on unit. From the results obtained it is reported that the maximum fruit set (78.68%), maximum fruit retention (61.67%) and minimum fruit drop (44.99%) with maximum length of fruit (6.00cm), diameter of fruit (4.50cm), fruit weight (21.45g), pulp weight (19.20g), yield (110.30kg/plant), total sugars (14.26%) and total soluble solids (20.55^{O}Brix) with minimum cracking (2.70%), rindand seed weight (2.06g and 2.05g, respectively) were recorded in the fruits which were produced from the plants treated with the foliar application of boron @ 0.6% and NAA @ 40ppm in the plains of North India.

Keywords: *Litchi, Boron, NAA, Fruit set, Fruit drop, Retention, Yield and physico-chemical quality.*

INTRODUCTION

The litchi (*Litchi chinensis* Sonn.) is a major subtropical evergreen fruit which belongs to the family Sapindaceae, having somatic chromosome number of 2n=30. It is believed that litchi originated in southern China. It is commonly assumed that litchi was introduced in India (West Bengal) through Burma at the end of the 18th century. Botanically the mature fruit of litchi is a nut and the edible part is fleshy aril. Due to the high sugar content in litchi, it is also called "Natural rasgullah". The sugar content varies from 6.74 to 18.0 per cent in Indian cultivars.

Apart from sugar, litchi is also a good source of vitamin 'C' (varying from 40.0 to 90 mg/100g), protein (0.8 to 0.9%), fat (0.3%), pectin (0.43%), and minerals, particularly calcium, phosphorus and iron (0.7%).

Boron is an essential element in preserving conducting tissue and it regulates another element and is also involved in reproduction, germination of pollen tubes and fertilization. In case of boron deficiency, flowers are produced least and more sterile, fruits are malformed and render themselves commercially useless. Boron deficiency induced a decrease in the amount of Ca associated with pectin constituents. Most of the boron in the pectin fraction obtained by pectin's treatment was found in a free form, suggesting that boron plays an important role in Ca metabolism in the cell wall. Naphthalene acetic acid (NAA) boosted fruit set; reduced fruit drop and improved the quality of fruits. Keeping the above facts in view, the present experiment was carried out to investigate the influence of different levels of boron and NAA on fruiting, yield and quality attributes of litchi in plains of North India.

MATERIALS AND METHODS

The present experiment was conducted in the Garden, Department of Fruit Science, Chandra Shekhar Azad University of Agriculture and Technology Kanpur from January to June 2023. The experiment was planned with sixteen treatments *viz.,* T_1 (20 ppm NAA), T_2 (30ppm NAA), T_3 (40ppm NAA), T_4 (0.2% boron), T_5 (0.2% boron + 20ppm NAA), T_6 (0.2% boron + 30ppm NAA), T_7 (0.2% boron + 40ppm NAA), T_8 (0.2% boron), T_9 (0.4% boron + 20ppm NAA), T_{10} (0.4% boron+ 30ppm NAA), T_{11} (0.4% boron + 40ppm NAA), T_{12} (0.6% boron), T_{13} (0.6% boron+ 20ppm NAA), T_{14} (0.6% boron + 30ppm NAA), T_{15} (0.6% boron+ 40ppm NAA) and T_{16} (control water spray), replicated thrice in Factorial Completely Randomized Design. Uniform and healthy plants of litchi cv. Dehradun was selected and each plant with similar three branches was identified and that was used as an unit. Each branch was allotted to one treatment with proper randomization.

Different levels of Boron, as well as NAA sprays, were done twice *i.e.,* first before flower initiation (6 February 2023) and second at pea stage (22 March 2023). All the manurial requirements, cultural practices and plant protection measures were adopted as per the recommendation and requirements. Five panicles in each direction were selected randomly in each treatment for recording fruiting and yield observation. Observations on fruit set, drop, retention, and cracking percentages were recorded during the fruiting season. At each picking, data on fruit weight and marketable yield per plant were recorded using a weighing balance. The length and diameter of ten randomly selected fruits were measured with the help of a Vernier caliper and expressed in cm, data on pulp weight, fresh weight of seed, and rind weight were recorded and expressed in grams (g). The total soluble solids content was determined with the help of Erma hand refractometer and total sugars was estimated according to the method as suggested in **A.O.A.C. (1980).**

RESULTS AND DISCUSSION

Fruit set (%):

The application of different concentrations of NAA and boron significantly affectes fruit set (Table 1). The maximum fruit set (64.77%) was recorded with the application of 0.6% boron, closely followed by 61.73% from 0.4% of boron application, while plants kept under control (untreated) showed minimum fruit set (55.32%). The maximum fruit set was recorded when the boron was used ina higher concentration. This increase in the fruit set may be due to the reason that boron is a micronutrient that improves plant nutrition

and pollen fertilization, which accelerates fruit set in the litchi plant. These findings are in agreement with the reports of **Sharma *et al.*, (2005), Gupta *et al.,* (2022)** in litchi and **Badal and Tripathi (2021b)** in guava.

Plants treated with the foliar application of NAA, the maximum fruit set (78.68%) was found in plants treated with NAA 60ppm, closely followed by 67.18% fruit set which were recorded from N_2 (40ppm NAA) treatment, whereas, the minimum fruit set (40.85%) was recorded in plants kept under N_0 (control) treatment. Higher fruit set with the application of NAA is due to the formation of sugar from polysaccharides and decrease in acid content during maturity and ripening period, which are mostly affected by auxin and these metabolic changes in the present investigation might have been helped improved incresed fruit set. These findings are in line with the reports of **Tripathi and Viveka Nand (2022)**in anola**, Quereshi *et al.*, (2011) and Sahay *et al.*, (2018)** in Litchi.

The interaction effect of boron and NAA application was not found to be significant, but there was an improvement in fruit set over the main effect was reported. The maximum fruit set (83.86%) was found with the application of 0.6% boron + 40ppm NAA (B_3N_3) followed by 77.33% with the application of 0.2% boron + 40ppm NAA, whereas, the minimum fruit set (36.30%) was recorded under control (B_0N_0). Higher fruit set is due to the reason that NAA strengthening the ability of fruit peduncle attached, which is to the root point of the fruit, finally preventing fruit drop. These findings are in agreement with the reports of **Quershi *et al.*, (2011) and Sahay *et al.*, (2018)** in litchi.

Fruit drop and fruit retention (%):

Boron concentrations gradually reduce fruit drop and increase fruit retention percentage and plants treated with 0.6% of boron showed significantly minimum (55.99%) fruit drop and maximum fruit retention (44.00%) followed by B_2 (0.4%) recording 60.50% of fruit drop and 39.49% of fruit retention (Table 1). Untreated plants *i.e.,* control results significantly maximum fruit drop (65.28%) and minimum fruit retention (34.71%) during 2022-23. This reduction of fruit drop and increase in fruit retention in litchi plants might be due to the reason that borax is an important part in the formation of middle lamella which is an important part of plant cells along with calcium pectate which plays an important role in the strengthening of pedicel attached to the proximal end of fruit which resulted in less fruit drop. Similarly, the reduction in fruit drop by the spray of borax may also be due to the indirect action of boron in auxin synthesis that delayed the formation of the abscission layer during the early stages of fruit development, which ultimately increases fruit retention percentage. These findings align with the results of **Saraswat *et al.*, (2006), Gupta *et al.,* (2022)** in litchi, **Maurya *et al.*, (2020)** in mango and **Tripathi *et al.,* (2018)** in aonla.

Fruit drop and fruit retention (at maturity stage) were influenced significantly with NAA treatment and the maximum fruit drop (69.51%) was recorded when the plants were treated with 20ppm of NAA and maximum fruit retention of 55.00% occurred under the treatment of 40ppm NAA during investigation. The minimum (44.99%) fruit drops were seen under NAA 40ppm treatment and fruit retention of 32.89% was achieved in plants kept under control (N_0) during investigation period. It is commonly known that when auxin concentration rises, low fruit production is caused by low auxin levels and lack of ultimate cell fracturing in the middle lamella or close to the abscission layer. By inhibiting the enzymes that make pectin soluble, auxin treatment to the fruits inhibits these alterations in the middle lamella, resulting in minimized fruit drop and

improved fruit retention. These findings are in consonance with the results of **Lal *et al.*, (2015)** in kinnow mandarin, **Tiwari *et al.*, (2017), Tripathi and Viveka Nand (2022)** in aonla and **Quershi *et al.*, (2011)** in litchi.

The interaction effect between Boron × NAA was found significant with respect to fruit drops and fruit retention and boron 0.6% with 40ppm of NAA (B_3N_3) results minimum fruit drop (38.33%) and maximum fruit retention (61.67%), whereas, maximum fruit drop (74.53%) and minimum fruit retention (25.47%) per panicles was recorded under control. Other treatment combinations also reduce fruit drop and maximize fruit retention as compared to control. These findings are in line with the reports of **Sahay *et al.*, (2018)** in litchi.

Cracked fruits percentage:

During present investigation period use of boron minimizes the number of cracked fruits and a minimum of 7.87% cracked fruits were noted under 0.6% (B_3) treatment, while a maximum of 14.22% cracked fruits were observed under untreated plants (B_0). The range of cracked fruits was indicated from 14.22 to 7.87 during the investigation period. It is well known that application of borax with other micronutrients regulate auxin contents in the plants which might have increased the synthesis of tryptophan and indirectly also regulated water relations in plants. The application of auxin might have increased the osmotic pressure of the cell sap,which will induce water uptake and reduce the cracking percentage in fruits. The findings are in accordance with the reports of **Katiyar *et al.*, (2008), Banyal and Rangra (2011), Gupta *et al.*, (2022)** in litchi.

The application of NAA concentrations had an impact on fruit cracking, and its 40 ppm concentration greatly reduced (3.79%) fruit cracking, whereas maximum (18.63%) fruit cracking was recorded under control. Similar to cellulose, hemicellulose and pectin which produce cell enlargement by decreasing the wall pith. This physiological effect of auxin may therefore reduce the cracking of fruit. These findings are in the support with the findings of **Saraswat *et al.*, (2006), Quershi *et al.*, (2011) and Sahay *et al.*, (2018)** in litchi.

The interaction between boron and NAA significantly reduced the number of cracked fruits and a minimum of 2.70% cracked fruits were recorded in the interactive treatment of 0.6% boron with 40ppm NAA (B_3N_3) followed by 0.4% boron and 40ppm NAA (B_3N_2) showing 2.50% cracked fruit in litchi and a maximum of 23.56% cracked fruits as recorded under control (B_0N_0). These findings are in line with the reports of **Saraswat *et al.*, (2006) i**n litchi and **Khatri *et al.* (2001)** in pomegranate.

Fruit length and diameter (cm)

Application of boron significantly influenced fruit length and fruit diameters with different concentrations. Significantly maximum (4.40cm) fruit length was recorded in treatment produced from plants kept under 0.6% (B_3) treatment, whereas, maximum fruit diameter (3.72cm) was recorded an treatment from the plants kept under B_2 (0.4% boron) treatment. Untreated plants showed minimum effectiveness with respect to fruit length and fruit diameter *i.e.,* 3.67cm and 2.80cm, respectively during investigation period. Boron have a substantial impact on fruit size enhancement due to its role in promoting cell elongation and expansion, which may led to a desired increase in the size of litchi fruits during present investigation period. These findings are in line with the reports of **Sharma *et al.*, (2005), Verma *et al.*, (2021)** in strawberry**, Gupta *et al.*, (2022)** in litchi and **Shukla *et al.*, (2011)** in aonla.

NAA have consistently and favorably effect on increase in fruit length and diameter. The average fruit length during the experimentation period was 5.47cm, with an average fruit diameter 3.90cm, which were recorded in 40ppm concentration (N_3), which shown to be the most responsive treatment. The smaller fruits, measuring 2.90 and 2.52cm in length and diameter, respectively are in plants kept under control (N_0). Fruit ranged from 2.90 to 5.47cm in length and 2.52 to 3.90cm in diameter in others treatments. The superiority brought about by NAA treatment may be attributable due to the substance's role in cell division, cell elongation and increased intracellular space which increase volume in the mesocarpic cells. Naphthalene acetic acid (NAA) increases the growth rate of fruits which results in bigger fruit size without any undesirable reduction in yield. The findings are in agreement with the reports of **Sahay *et al.*, (2018)** in litchi and **Badal and Tripathi (2021a)** in guava.

The length and diameter of litchi fruits were significantly influenced by the interactive treatment of Boron x NAA. Significantly, B_3N_3 had the maximum fruit length and diameter of 6.40cm and 4.50cm, respectively, followed by B_2N_3 (6.50cm and 4.20cm, respectively). Under interactive control, the minimum fruit dimensions of 2.60 cm in length and 2.30 cm in diameter were noted. These findings are in line with the reports of **Kumar and Tripathi (2009)** in strawberry and **Singh *et al.*, (2012)** in aonla.

Fresh weight and pulp weight(g):

Boron nutrition positively influenced fresh fruit weight and pulp weight and its 0.6% (B_3) concentration induced maximum fresh fruit weight and pulp weight*i.e.,* 18.43 and 15.52g, respectively, whereas, the minimum 16.41 and 13.70g, respectively were recorded in the fruits produced from the plants kept under B_0 (control). These findings are in accordance with the reports of **Maurya *et al.,* (2020)** in mango, **Banyal and Rangra (2011), Gupta *et al.,* (2022)** in litchi.

Similarly, treatments of NAA also influenced fresh fruit weight and pulp weight and significantly maximum fruit weight (21.37g) and pulp weight (18.45g) were recorded in fruits which were produced plants treated with 40ppm of NAA (N_3) and it was closely followed by the N_2 (30ppm NAA) which produced *i.e.*, 1.59 and 16.55g, respectively. The plant kept under control showed significantly minimum fruit weight and pulp weight *i.e.* 12.99 and 10.05g, respectively during 2022-23. Auxin plays a very important role in cell wall elasticity and flexibility is one of the major sources of evidence to affect fruit weight and pulp weight. These findings are in line with the reports of **Badal and Tripathi (2021a)** in guava.

The interactive effect of boron and NAA did not bring a significant effect in respect to fruit weight and pulp weight. But further improvement over the main effect was recorded and B_3N_3 combination exhibited maximum fruit weight and pulp weight (21.45 and 19.45g, respectively). The control showed the lowest amount for fruit weight and pulp weight *i.e.,*11.62 and 9.10g, respectively, during the experimentation period.

Fresh seed weight and rind weight (g):

Boron treatments affect the fresh weight of seed and rind weight with different doses. Significantly minimum (2.92g) seed weight and maximum rind weight (1.01g) were recorded in fruits which were produced from the plants kept under 0.6% boron (B_3) treatment, whereas, maximum seed weight (3.24g) and minimum rind weight (0.80g) were recorded under control. Boron increased the pulp content litchi fruit, which may have led to a reduction in the weight of the seeds in the litchi fruits. These findings are in agreement with the reports of **Saraswat *et al.*, (2006),** and **Gupta *et al.,* (2022)** in litchi.

NAA also showed effectiveness with different concentrations and the heaviest seed weight (3.72g) was found in fruits which were produced from the plants kept under control with minimum (0.07g) rind weight. The smaller seed weight (2.26g) was noted under 40ppm NAA and maximum rind weight *i.e.,* 1.83g was expressed under N_3 (40ppm NAA) during the year of investigation. Increased cell flexibility and plasticity brought by NAA encouraged cell wall stretching and increased water uptake, both of which may have increased pulp weight while decreasing seed weight. These findings are in line with the reports of **Saraswat *et al.*, (2006)** in litchi.

The interactive effect of boron and NAA caused significant variation in seed weight and rind weight of litchi. The maximum seed weight and rind weight of 3.73 and 2.06g, respectively were observed under control (B_0N_0), whereas minimum rind weight (0.05g) and seed weight of 2.06g were weighted under B_3N_3 (0.6% boron and 40ppm NAA) treatment. Boron reduced interveinal chlorosis in leaves, which had a good effect on plant growth and development. It also played a significant role in photosynthesis in plants, which increased the sugar content of fruits and may have helped to increase fruit weight, rind weight, and pulp weight and decreased seed weight. These findings are in line with the reports of **Saraswat *et al.*, (2006)** in litchi.

Marketable yield (kg/plant):

The foliar spray of micronutrient *i.e.,* boron considerably increased the production of marketable fruits and a significantly maximum (96.67 kg) fruit yield per plant was expressed under plants treated with 0.6% boron (B_3) followed by 91.90 kg yield per plant was found under 0.4% boron (B_2), whereas lowest yield 87.17kg of marketable fruit per plant was exhibited under control [Fig 1(a and b)]. Boron aids in the movement of metabolites from source to sink, which increases the retention of more fruits on trees which ultimately increases fruit yield in plants. These findings are in accordance with the reports of **Katiyar *et al.*, (2008), Saraswat *et al.*, (2006), Gupta *et al.,* (2022)** in litchi, **Tripathi and Viveka Nand (2022)** in anola.

All the cracked and other blemished fruits were isolated from the overall yield of litchi fruit in order to calculate the yield of marketable fruit. Under the treatment of NAA 40ppm, yield per plant was significantly maximum, indicating 107.37 kg. When the plants received no NAA treatment gave minimum of 73.47kg marketable fruits per plant in control (N_0). During the experimental period, the yield of marketable fruit varied from 73.47 to 107.37kg in other treatments. The benefit caused by NAA may be related to its physiological actions in the plants, which may have prevented fruit drop, reduced cracking, and significantly decreased the quantity of imperfect fruits, improving production and marketable yield. The above findings are in line with the reports of **Yadav *et al.*, (2010)** in aonla and **Saraswat *et al.*, (2006)** in litchi.

A maximum marketable yield of 110.30kg per plant was observed under the interaction treatment of B_3N_3(0.6% Boron and 40ppm NAA), whereas, a minimum (70.40kg/plant) was recorded under control (B_0N_0). These findings are in line with the reports of **Dutta and Banik (2007)** in guava and **Saraswat *et al.*, (2006)** in litchi.

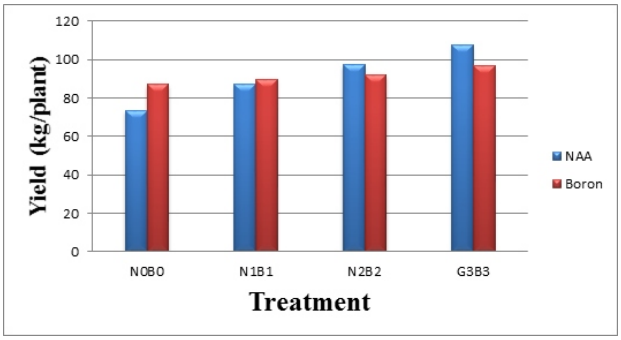


Fig. 1 (a): Effect of NAA and boron on yield (kg/plant).

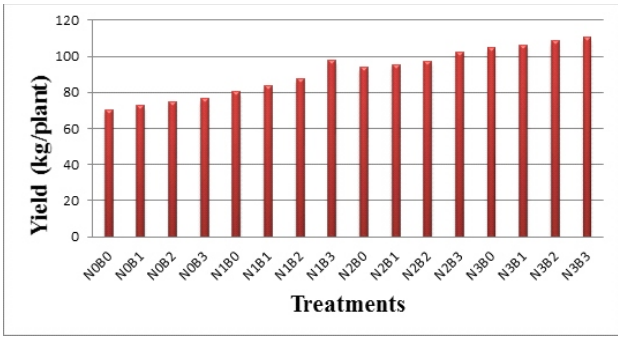


Fig. 1 (b): Effect of NAA, boron and their interaction on yield (kg/plant)

Quality attributes:

Total sugars (%):

Fruit produced from the concentration of 0.6% boron (B_3) treated plants recorded a maximum of 12.73% total sugars as compared to other treatments. On the untreated plant *i.e.,* control (B_0) treatment achieved minimum of 12.27% of total sugars. In this regard, a range of 12.27 to 12.73% was observed in other treatments. The conversion of starch and acid into sugars, as well as the ongoing mobilization of sugars from leaves to fruits may be the cause of the rise in total sugars in fruit pulp caused by boron foliar sprays. The present findings and in line with the reports of **Rawat *et al.*, (2010)** in guava**, Kumar *et al.*, (2017)** in aonla, **Saraswat *et al.*, (2006) and Priyadarshi *et al.*, (2018), Gupta *et al.*, (2022)** in litchi.

The total sugars content of litchi fruit was altered by the foliar sprays of NAA @ 40ppm and it was recorded maximum (13.92%) as compared to the control (N_0), where it was found to be minimum *i.e.*, 11.46 %. Less sugar was accumulated in NAA values that were lower or higher than 40 ppm. Another possible explanation for the rise in total sugars is the conversion of stored starch and other polysaccharides into soluble sugars. These findings are in accordance to the reports of **Saraswat *et al.*, (2006)** in litchi, **Lal *et al.*, (2016)** in kinnow.

The interaction effect among the foliar spray of Boron and NAA improved significantly total sugars content in litchi fruits. The maximum (14.26%) total sugars was found under B_3N_3 (0.6% boron + 40ppm NAA) followed by 14.14% under N_3B_2. The minimum total sugars content 10.86% was observed infruits produced from the plants kept under control (B_0N_0). These findings are in agreement with the reports of **Saraswat *et al.*, (2006)** in litchi.

Total soluble solids (^{0}Brix):

Application of Boron @ 0.6% (B_3) was recorded highest total soluble solids content (19.32^{0}Brix) followed by 19.13^{0}Brix of total soluble solids with 0.4% boron (B_2), while, control (B_0) treatment sowedthe lowest total soluble solids (18.77^{0}Brix). Due to sprays of 40ppm of NAA, increased total soluble solids contentby 5.26%. Increased total soluble solids content due to the application of boron might be its role in the hydrolysis of complex polysaccharides into simple sugar, the synthesis of metabolites and the rapid translocation of minerals and products used in photosynthetic processes from one area of the plant to another, including the developing fruits. The present results are in line with the reports of **Rawat *et al.*, (2010)** in guava, **Saraswat *et al.*, (2006), Katiyar *et al.*, (2008), Gupta *et al.*, (2022)** in litchi **and Kumar *et al.*, (2017)** in aonla.

Foliar application of NAA significantly increases total soluble solids content. When a plant is treated with 40ppm NAA (N_3) produced fruits having maximum total soluble solids (20.32^{0}Brix), whereas, the minimum total soluble solids (17.73^{0}Brix) was obtained under control (N_0). The enhancement in total soluble solids content ranged from 17.73 to 20.32^{0}Brix in other treatments. The increase in amylase activity, which led to the conversion of starch into simple sugar and increased the total soluble solids content of

fruits, may have contributed to the improvement in total soluble solids with the use of the growth regulator NAA. The findings are in accordance with the reports of **Kumar and Tripathi (2009) in** strawberry, **Lal *et al.*, (2016)** in kinnow and **Dodiya *et al.*, (2018)** in guava.

Interactive effect among foliar application of boron and NAA, not influence total soluble solids content significantly but maximum total soluble solids (20.55^{0}Brix) was found in fruits produced from the plants treated with 0.4% boron and 40ppm NAA (B_2N_3), while the minimum total soluble solids (17.55^{0}Brix) was recorded under control (B_0N_0) treatment. Increased total soluble solids content with the application of boron may be due to its role in the hydrolysis of complex polysaccharides into simple sugar and increased the total soluble content of fruits, which may have contributed to the improvement in total soluble solids with the use of the growth regulator NAA. The findings are in accordance with the reports of **Saraswat *et. al.*, (2006)** in litchi and **Rawat *et. al.*, (2010)** in guava.

Table1 : Effect of foliar sprays of Boron, NAA, and their interaction on fruiting and physical characters of litchi cv. Dehradun

Treatment	Fruit set (%)	Fruit drop (%)	Fruit retention (%)	Fruit cracking (%)	length of fruit (cm)	Fruit diameter (cm)
B_0	55.32	65.28	34.71	14.22	3.67	2.80
B_1	58.12	61.02	38.97	12.93	3.42	2.85
B_2	61.73	60.50	39.49	9.18	4.32	3.72
B_3	64.77	55.99	44.00	7.87	4.40	3.10
S.E.(m)±	**0.47**	**0.42**	**0.30**	**0.09**	**0.028**	0.018
CD at 5%	**1.38**	**1.22**	**0.88**	0.28	**0.082**	**0.10**
N_0	40.85	67.10	32.89	18.63	2.90	2.52
N_1	53.21	69.51	30.48	14.34	3.15	3.25
N_2	67.18	61.20	38.80	7.44	4.30	2.80
N_3	78.68	44.99	55.00	3.79	5.47	3.90
S.E.(m)±	**0.47**	0.42	0.30	0.09	**0.028**	0.018
CD at 5%	**1.38**	1.22	0.88	0.28	**0.082**	**0.10**
B0N0	36.30	74.53	25.47	23.56	2.60	2.30
B0N1	48.40	71.56	28.44	19.36	3.30	3.30
B0N2	63.40	62.40	37.60	8.53	4.30	2.30
B0N3	73.20	52.66	47.34	5.46	4.50	3.30
B1N0	39.36	66.53	33.47	22.33	2.60	2.30
B1N1	50.36	70.63	29.37	17.36	2.40	3.20
B1N2	65.43	60.60	39.40	7.50	4.20	3.30
B1N3	77.33	46.33	53.67	4.53	4.50	3.60
B2N0	42.40	72.66	27.34	15.30	3.10	3.20
B2N1	55.60	68.20	31.70	11.43	3.40	4.20
B2N2	68.56	58.50	41.50	7.50	4.30	3.30
B2N3	80.36	42.66	57.34	2.50	6.50	4.20
B3N0	45.36	54.70	45.30	13.33	3.30	2.30
B3N1	58.50	67.66	32.34	9.23	3.50	2.30
B3N2	71.36	63.30	36.70	6.23	4.40	3.30
B3N3	83.86	38.33	61.67	2.70	6.40	4.50
S.E.(m)±	**0.47**	**0.84**	**0.61**	**0.19**	**0.057**	0.03
CD at 5%	**NS**	**2.44**	**1.77**	**0.57**	**0.164**	0.10

Table2: Effect of foliar spray of Boron, NAA and their interaction on yield and quality attributes of litchi cv. Dehradun

Treatment	Fresh weight of fruits (g)	Pulp weight (g)	Fresh weight of seed (g)	Rind weight(g)	Total sugars (%)	TSS content (°Brix)
B_0	16.41	13.70	3.24	0.84	12.27	18.77
B_1	17.38	14.75	3.05	0.80	12.71	18.89
B_2	18.09	15.05	2.97	0.89	12.84	19.13
B_3	18.43	15.52	2.92	1.01	12.73	19.32
S.E.(m)±	**0.144**	**0.229**	0.023	0.009	**0.116**	0.140
CD at 5%	**0.418**	**0.663**	0.066	0.027	**0.335**	0.406
N_0	12.99	10.05	3.72	0.07	11.46	17.73
N_1	16.37	14.97	3.41	0.29	12.29	18.56
N_2	19.59	16.55	2.79	1.35	12.88	19.50
N_3	21.37	18.45	2.26	1.83	13.92	20.32
S.E.(m)±	**0.144**	**0.229**	0.023	0.009	**0.116**	0.140
CD at 5%	**0.418**	**0.663**	0.066	0.027	**0.335**	0.406
B0N0	11.62	9.10	3.73	0.05	10.86	17.55
B0N1	14.43	12.30	3.41	0.15	12.14	18.36
B0N2	18.36	15.30	3.18	1.55	12.66	19.06
B0N3	21.26	18.10	2.65	1.62	13.44	20.14
B1N0	12.48	9.50	3.73	0.06	11.95	17.58
B1N1	16.36	12.32	3.41	0.23	12.18	18.38
B1N2	19.34	16.20	2.85	1.13	12.86	19.36
B1N3	21.36	18.10	2.21	1.81	13.85	20.26
B2N0	13.48	10.30	3.72	0.07	11.96	17.85
B2N1	17.27	14.20	3.41	0.37	12.33	18.66
B2N2	20.21	17.30	2.65	1.29	12.96	19.66
B2N3	21.42	18.40	2.12	1.86	14.14	20.36
B3N0	14.40	11.30	3.72	0.13	11.07	17.95
B3N1	17.43	14.20	3.42	0.42	12.53	18.85
B3N2	20.46	17.40	2.50	1.46	13.07	19.95
B3N3	21.45	19.20	2.06	2.06	14.26	20.55
S.E.(m)±	**0.289**	**0.45**	**0.046**	**0.018**	**0.232**	0.281
CD at 5%	**0.836**	**1.32**	**0.132**	**0.053**	NS	NS

Conclusions:

Based on the findings of this study, it can be stated that individual applications of boron and NAA caused significant alterations in plant metabolism. Fruit set, retention, length, diameter, weight, pulp weight, rind weight, marketable yield, total sugars, and TSS content are enhanced with the application of boron @ 0.6%. Other features, such as cracked fruits and fruit drop per cent have also been reduced with this treatment. Application of NAA 40ppm was found more effective in enhancing fruit set, fruit retention, length of fruit, freshweight of fruit, pulp weight, marketable yield and total soluble solids content and it also minimized fruit drop, cracked fruit and seed weight. Boron @ 0.6% in association with NAA 40ppm was more effective in increasing fruit length, diameter, marketable yield, total sugars and total soluble solids content and minimized rind weight and cracked fruits in litchi. As a result of the foregoing experiment, litchi growers are prescribed to use boron @ 0.6% with NAA @ 40ppm to improve the quality and output of litchi fruits in the plains of North India.

REFERENCES

1. **A.O.A.C. (1980).** Official Methods of analysis, Association of Official Analytical Chemists, Washington, D.C., U.S.A.
2. **Badal, D. S. and Tripathi,V. K. (2021a).** Effect of foliar application of NAA and Boron on physico-chemical parameters of winter season guava *(Psidium guajava* L.) cv. Lucknow-49. *The Pharma Innovation Journal*, **10**(9): 928-932.
3. **Badal, D. S. and Tripathi,V. K. (2021b).** Influence of foliar feeding of NAA and Boronon growth, flowering, fruiting, and yield of winter season guava (*Psidium guajava* L.) cv. L-49. *Biological Forum-An International Journal,* **13**(3): 387-391.
4. **Banyal, A. K. and Rangra, A.K. (2011).** Response of yield and quality attributes of litchi *cv.* Dehradun to soil and foliar application of boron. *Journal of Hill Agriculture*, **2**(1): 33-37.
5. **Dodiya, K.D., Dalvadi, A.C., Halepotara, F.H. and Solanki, P.S. (2018).** Effect of foliar application of plant growth regulators and boron on quality of Guava (*Psidium gujava* L.) cv. L-49. *International Journal Chemical Studies*, **6**(3): 1396-1398.
6. **Dutta, P. and Banik, A. K. (2007).** Effect of foliar feeding of nutrients and plant growth regulators on physico-chemical quality of Sardar guava grown in red and lateritic tract of West Bengal. *International GuavaSymposium,***735:** 407-411.
7. **Gupta, A., Tripathi, V. K. and Shukla, J. K. (2022).** Influence of GA_3, Zinc and Boron on fruit drop, yield and quality of litchi *(Litchi chinensis Sonn.). Biological Forum-An International Journal*, **14**(3): 1079-1083.
8. **Katiyar, P.N., Prakash, O., Singh, J.P. and Singh, P.C. (2008**). Effect of zinc sulphate, borax and calcium nitrate on flowering, fruiting, yield and quality of litchi cv. Dehradun. *Journal of Rural Agriculture Research,* **8**(2): 49-51.
9. **Khatri, K., Joon, M.S. and Singh. R. P. (2001).** Effect of micronutrient and growth regulators on premature and mature cracking of Pomegranate var. Jodhpur Red. *Haryana Journal of Horticulture Science,* **30**(3-4): 207-208.
10. **Kumar, A., Tripathi, V. K., Dubey, V., Katiyar, N. K. and Tiwari, P. (2017).** Influence of foliar application of calcium, zine and boron on fruit drop, yield and quality attributes of Aonla (*Emblica officinalis*) cv. NA-7. *Research on Crops,* **18**(1):91-97.
11. **Kumar, R. and Tripathi,V. K. (2009).** Influence of NAA, GA_3 and Boric Acid on growth, yield and quality of strawberry cv. Chandler. *Progressive Horticulture,* **41**(1): 113-115.
12. **Lal, D., Tripathi, V. K., Kumar, S. and Nayyer, M. A. (2015).** Effect of Pre-harvest Application of Gibberellic Acid, NAA and Calcium Nitrate on fruit drop, maturity and storage quality ofKinnow Mandarin. *Res. Environ Life Science,* **8**(4) 561-564.
13. **Lal, D., Tripathi, V. K., Nayyer, M. A., Kumar, S., Ahmed, M. and Siddiqui, M. W. (2016).** Pre-harvestspray of Gibberellic Acid, NAA, and Calcium Nitrate on fruit retention, yield and quality of Kinnow Mandarin. *Environment & Ecology,* **34**(4C): 2288 2292.
14. **Maurya, P. K., Tripathi, V. K. and Gupta, S. (2020).** Effect of pre-harvest application of GA_3, Naphthalene acetic acid and borax on fruit drop, yield and quality of Mango cv. Amrapali. *Journal of Pharmacognosy and Phytochemistry,* **9**(6), 2123-2127.
15. **Priyadarshi, V., Hota, D. and Kumar, K. A. (2018).** Effect of growth regulators and micronutrient spray on chemical parameters of litchi (*Litchi chinensis* Sonn.) cv. Calcuttia. *International Journal of Economic Plants*, **5**(3): 99-103.
16. **Qureshi, S. N., Rather, J. A. and Bhat, S. K. (2011).** Effect of exogenous auxin application on fruit drop and fruit cracking in Litchi (*Litchi chinensis* Sonn.) cv. Dehradun. *Environment and Ecology,* **29**(1): 235-237.
17. **Rawat, V., Tomar, Y.K., Rawat, J.M.S. (2010).** Influence of foliar application of micro nutrient on the fruit quality of guava cv. Lucknow-49. *Journal of Hill Agri*culture, **1**(1):63-66.
18. **Sahay, S., Kumari, P., Mishra, P.K., Rashmi, K., Shrivastava, P., Ahmad, Md. F. and Kumar, R. (2018**). Pre-harvest foliar spray of micronutrients and growth regulators on yield attributes of litchi (*Litchi chinensis* Sonn.) 'Purbi'. *Acta Horticulture,* **1211**:19
19. **Saraswat, N. K., Pandey, U. N. and Tripathi, V.K. (2006).** Influence of NAA and Zinc sulphate on fruit drop, cracking, fruit size, yield and quality of litchi cv. Calcuttia. *Journal of Asian Horticulture*, **2**(4): 255-259.
20. **Sharma, P., Singh, A.K. and Sharma, R.M. (2005).** Effect of plant bio-regulators (PBRs) micro-nutrients on fruit set, quality of litchi cv. Dehradun. *Indian Journal of Horticulture*, **62**(1): 24-26.
21. **Shukla, H. S., Kumar,V. and Tripathi, V. K. (2011).** Effect of Gibberellic Acid and Boron on development and quality of aonla fruits 'Banarasi'. *Acta Horticulturae,* **890:**375-380.
22. **Singh, P.C., Gangwar, R.S. and Singh, V.K. (2012).** Response of boron, zinc and copper on quality of Aonla fruit cv. Banarasi. *Horticulture Research Spectrum*, **1**(1): 89-91.
23. **Tiwari, P., Tripathi, V.K. and Singh, A. (2017).** Effect of foliar application of plant bio-regulators and micronutrients on fruit retention, yield and quality attributes of aonla. *Progressive Research-An International Journal,* **12** (Special-IV): 2565-2568.
24. **Tripathi, V. K. and Viveka Nand (2022).** Effect of foliar application of Boron, Zinc and NAA on fruit retention, yield and quality attributes of Aonla. *Progressive Horticulture*, **54**(1): 76-81.
25. **Tripathi, V. K., Pandey, S. S., Kumar, A., Dubey, V. and Tiwari, P. (2018).** Influence of foliar application of gibberellic acid, calcium and boron on fruit drop, yield and quality attributes of aonla (*Emblica officinalis*) cv. NA-7. *Indian Journal of Agricultural Sciences, 88*(11): 1784-1788.

26. **Verma, S., Dwivedi, A.K. and Tripathi, V. K. (2021).** Effect of gibberellic acid and boron on growth, yield and yield attributory traits in strawberry (*Fragaria* x *ananassa*Duch.) under North Gangetic Plains. *Biological Forum-An International Journal,* **13**(3): 262-267.

27. **Yadav, S., Shukla, H.S. and Ram, R.A. (2010).** Studies on foliar application of NAA, GA_3, Boric acid and $Ca(NO_3)_2$ on fruit retention, growth, yield and quality of Aonla (*Emblica officinalis* Gaertn.) cv. Banarasi. *Horticulture Journal*, **23**(2): 64-67.

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SYNTHESIS & CHARACTERIZATION OF SCHIFF'S BASE DERIVED FROM 2-AMINO-4-(FLUOROPHENYL) THIAZOLE AND SALICYLALDEHYDE AND THEIR FEW TRANSITION METAL COMPLEXS

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ABSTRACT

A series of new complexes involving Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) ions and Schiff's base ligand obtained by condensation of 2-amino-4-(fluorophenyl) Thiazole and salicylaldehyde have been synthesized. The complexes are characterized by elemental analysis, magnetic susceptibility, IR and electronic spectral studies. The IR spectral study shows that azomethinic nitrogen and oxygen of phenolic group are taking part in co-ordination. All the complexes are having octahedral geometry. These complexes were also screened for their fungicidal activity against *Phoma-exigua, Macrophomino-phaseoli* and _*Colletotrichum* by Growth method.

INTRODUCTION

Transition metal complexes of Schiff's bases are the most widely studied coordination compound because they can be used as biochemical analytical and antimicrobial reagent[1-3] . Metal complexes with ligands, capable of coordination with two or more sites with metal ion have evolved much interests in the field of coordination chemistry. The present paper deals with the preparation and characterization of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes with Schiff's base derived by condensation of 2-Amino-4-(Fluorophenyl) Thiazole with salicylaldehyde. The ligand and their metal complexes with Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Fe(II) metal ions the ligand and the newly synthesized complexes were also screened for fungicidal activity against various fungi.

EXPERIMENTAL

Fluorobenzene was of G.S.C. grade and other chemical used were of BDH (A.R.) grade.

The infrared and for infrared spectra of these complex were recorded in KBR or nujol mull. The electronic spectra of the complexes were in MgO at room temperature on a VSU-22 spectrophotometer, IR and electronic spectra recorded at GND University, Amritsar. Magnetic measurement were carried out at Roorkee University at room temperature using Co [Hg(CNS)$_4$] as callibrant. The metal[2] and sulphur[3] contents of the complexes were determined using standard method reported in literature.

Fluroacetophenone was prepared from fluorobenzene using the procedure reported in

literature[4]. The ligand 2-amino-4-(p-fluorophenyl) thiazole was prepared using the standard method. The ligand was prepared by refluxing the mixed solution of thiazole (.01 mol) in 50 ml ethanol and salicylaldehyde (0.01 mol) in 15 ml ethanol. The mixed solution was refluxed for two hours on water bath. The reaction mixture was then allowed to cool and poured into ice. The ligand separated out which was filtered, washed with alcohol and dried.

PREPARATION OF COMPLEX

All the complexes were prepared by the refluxing the appropriate metal salt(0.01 mol) in 20 ml ethanol with 40 ml of ethanolic solution of ligand (0.01 ml) for three hours. The reaction mixture was cooled and kept for over night. Complexes separated which were filtered, washed and dried.

RESULT AND DISSUASION

The elemental analysis data shows that all the complexes are having 1:2 stoichiometry. The IR spectra of ligand on comparison with those of complexes is found that vC=N vibration in all complexes shows a shift to the lower side indicating coordination of azomethinic nitrogen of the ligand. This is also supported by the appearance of the bond corresponding to the metal nitrogen at 465-475 cm^{-1} in the complexes. The vC=O band shifted to higher frequency at 1305-1320 cm^{-1} in the complexes integrating co-ordination through the oxygen atom of the phenolic group. This is further supplied by the appearance of the band at 300-320 cm^{-1} due with the metal oxygen stretching vibration in the complexes.

The present Mn(II) complexes have magnetic moment around 5.5 B.M. whch is characterstic for the high spin octahedral complexes[6]. They have four weak bands in the 17500-18800, 21200-22000, 25000-26200 and 27900 cm^{-1} region arising from sextet from sextet quartet configuration and assignable to $^6A_{1g} \xrightarrow{\sqrt{1}} {}^4T_{1g}$, $^6A_{1g} \xrightarrow{\sqrt{2}} {}^4T_{2g(G)}$, $^6A_{1g} \xrightarrow{\sqrt{3}} {}^4T_{1g(G)}$, and $^6A_{1g} \xrightarrow{\sqrt{4}} {}^4T_{2g(D)}$ transitions, respectively. The magnetic value and electronic spectra support the octahedral configuration.

The electronic spectra of $Ni^{(11)}$ complexes show bands at 8500-9000 cm^{-1} 14580-15100 cm^{-1} characterstics for the octahedral Ni(II) ion. These band may be assigned to $^3A_{2g} \xrightarrow{\sqrt{1}} {}^3T_{2g(F)} \xrightarrow{\sqrt{2}} {}^3T_{2g(F)}$ and $^3T_{1g} \xrightarrow{\sqrt{3}} {}^3T_{1g(P)}$ respectively. The magnetic moment values are between 3.16 and 3.20 B.M. which show the presence of two unpaired electrons and is typical for octahedral Ni(II) complexes.

In the electronic spectra of Co(II) complexes three absorption bands were observed around 8900, 168700 and 18760 cm^{-1} these are assignable [7-9] to octahedral region. These band may be assigned to $^4T_{1g(F)} \xrightarrow{\sqrt{1}} T_{2g(F)} \xrightarrow{\sqrt{2}} {}^4A_{1g(F)}$ and $^4T_{1g(F)}$ respectively. The magnetic moment of Co(II) complexes were found tyo be 4.32-4.90 B.M. which is characterstic of high spin octahedral complexes.

The electronic spectra of Cu(II) complexes shows only one broad absorption band at 15800 cm^{-1} indicating probably a distorted octahedral configuration. The magnetic moment values of the Cu(II) complexes are in the range of 1.84 – 1.88 B.M.

Zn(II) complexes do not show d-d transitions hence their stereochemistry can not be determined from UV and visible reflectance spectra.

Low values of conductance (30-33 mhos cm^2 mol^{-1}) shows that Mn(II), Ni(II), Cu(II) and the chloro complexes of Co(II) are have conductance values in the 62-100 mhos cm^2 mol^{-1} range, they are non electrolytes, while Fe(II) and the acetate, nitrato and sulphato complexes of Co(II) electrolytes and the anions

are not co-ordinated to the metal ion.

The thermal studies show that all the complexes are thermally stable upto 120^0C and in every case the end product is a metal oxide.

FUNGICIDAL ACTIVITY

The fungicidal activity of the ligand as well as of the *Phomina-exigua*, *Macrophomina-phaseoli*, *Colletotrichum-capsici* at 100, 50 and 20 ppm in czapecks dox agar medium. From the fungicidal activity table 2 it is clear that the ligand itself is more toxic than the metal complexes and the fungicidal activity decearse with a decrease in concentration.

REFRENCES

1. B. Dash and M.K. Rout – J. Ind. Chem. Soc., 32, 663, (1955).
2. M.K. Rout and G.N. Mahapatra – J. Am. Chem. Soc., 76, 2427 (1955).
3. S.A. Ravizza, Neth – Appl., 6 138, 508, Chem. Abstr., 64, 17611 a (1966).
4. I. Saikawa and S. Takano – Japan, 70, 27, 973, Chem. Abstr., 74 3604 p (1971); 74 36075 (1971).
5. K. Thomae. G.m. b.H. Ger. – Offen, 1, 71, 918, Chem Abstr. 74, 31749 h (1971).
6. Dia- Nippon Drug Manufg. Co. – Japan, 7274 (1960); Chem. Abstr., 55, 6499d (1961).
7. L.W. Werbal, E.F. Elslager, A.R. Phillips, D.F. Worth, P.J. Islip and N.C. Neville – J. Med. Chem., 12, 521 (1969).
8. S.F. Dyke – The chemistry of vitamin's (Inter science), New York P.4. (1965).
9. R. Breslow – CIBA study group N. (Little Brown and Co., Boston) p. 65 (1968).
10. E.H. Northry – Chem. Revs., 27, 85 (1940).
11. M.R.A. Chance, P. Dirnhuber and F.A. Robinson, Brit. J. Pharmacol – Che. Revs. 27, 85 (1940) 1, 153 (1946).
12. J.C. Karntz and C.J. Carz. – Pharmacologic Principles of Medical practice, (Witliams and Wilkins Co.) 6, 865 (1967).
13. M.Y. Mhasalkar, M.H. Shah, K.G. Anant Narayan C.V. Delivala – J. Med. Chem. 14 (10), 260 (1971) 13 (4), 672 (1970).
14. E.J. Duff, M.N. Hughes K.J. Rutt – (a) J. Chem. Soc (A), 2354 (1969). (b) J. Chem. Soc. (A) 2101 (1969). (c) Inorg. Chim. Acta 6, 408 (1972).
15. W.J. Kilbeck, F. Holmes, A.E. Underhill – J. Chem. Soc. (A), 757 (1967).
16. R.A. Ford, G. Halkyard A.E. Underhill – Inorg. Nucl. Chem. Letters, 4, 507 (1968).
17. W.V. Malik, K.D. Sharam, R.D. Sharma J.S. Upodhaya, – Ind. J. Chem., 15 (A), 152 (1977).
18. R.N. Dash and D.V. Ramanarao – J. Ind. Chem. Soc, 51, 787. (1974).
19. J.A. Weaver, P. Hambright, P.T. Talbert, R. Kaug, and A.N. Thorpe, – Inorg. Chem., 9, 268 (1970).
20. Lenercik Beniamin, Kuling Jacel and Barszch Barbara, – Rocz, Chem. 48, 2111 (1974).

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PROMOTION AND INHIBITION OF SEEDLING GROWTH IN VIGNA RADIATA CVT 163 SEEDLING GROWTH IN DARK IN PRESENCE OF HEAVY METAL MANGANESE

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ABSTRACT

In the whole universe only earth planet is a place where living beings can survive the 75% part of earth containing water and remaining land is used by human beings for their living. The resources are limiting to consume by human beings for their living. The resources are limiting to consume by human beings but density of human beings rapidly increases and increasing in the interfering with environment. This is cause of pollution. Pollution is caused by all those hazardous substances added by man's activity in the environment. Which damage the ecological balance and causes harm to human health. Pollution is restricted to certain human activities. For instance affluent industrialized countries are dumping a lot of materials and wastes in their immediate environment. Effect of pretreatment of heavy metal Mn carried on seedling of Vigna radiata CVT 163 in dark. That show retardation of seedling growth in presence of higher concentration of Mn and acceleration of growth is the lower concentration of same metal.

Key words Vigna radiata, hybrid, manganese, heavy metal, seedling growth, environmental pollution.

INTRODUCTION

In present time environmental pollution is a major global crisis all our basic needs as air, water food surroundings etc. are one way or the other are highly polluted by different types of pollutants and toxic material present in the atmosphere.

The current stage of the earth that we are seeing is the cause of centuries of exploitation of earth and its resources. Moreover the earth can not restore its balance because of environmental pollution. The contamination of the physical and biological components of the earth system to such as extent that normal environmental processes are adversely affected. Pollution is the introduction of contaminates in to the natural environment that cause adverse change, pollution can take the form of chemical substances or energy such as noise heat or light pollutants the components of pollution can be either foreign substances or naturally occuring contaminants.

In the local area this is the major problem as polluted water is used for irrigation. Such irrigation practices do not have apparent

deleterious symptom on the crops, but lead to heavy metal accumulation in the edible parts of crop plants **Kumar (1978) Jain (1980) Sharma (1982) Agarwal (1989) Goel (1992) Verma (1993) and Bhargava (1996) Grove (1987)** reviewed that various aspects of atmosphere pollution through chemical pollutants. Toxic effects of high concentration Mn in field and garden crops summarized **(Lohnis 1951, Williams and Vlamis 1957)** Manganese toxicity in cotton also worked out **(Adam and Wear 1957) Souto and Doberneiner (1971)** summarized Mn toxicity in some legumes.

Accumulation of Mn in Tomato and onion seeds also reported **Traverse and Rickeless 1973 Vlamis and Williams (1973)** reported toxic effects of Mn in lettuce.

Toxic effect of Mn also worked out in Soyabean **(Brown and Jones 1977)** Toxic effect of high concentration of Mn have also been summarized in certain plants **(Strong et al 1985)** Toxicity of Mn in muskmelon also described **(Elomin and Wilex 1986)** The amount of the elements Mn P6, Si, N, P, Ca Na, Mg Fe, Sr, Zn and Cu in the reeds and in various specific organs Culms, leaves, adventitious roots, rhizomes roots and root hair) were studied at the bank of lake that are polluted by sewage and unpolluted banks.

Kozak and Tarkowaki (1979) studied magnese, copper, zinc iron and magnesium contents at different growth stages of tritloale, wheat and rye. **(Zuchajowska et al (1980)** observed accumulation of heavy metals in an ecosystem influenced by Zn-plant- emissions. **Say et al (1981)** observed aquatic mossess as monitors of heavy –metals contamination in river etherow, near Manchester, Great Britain UK **Vander Werff et al (1982)** studied in the long term experiment lasting up to 73 days the effect of rather low levels of Cu, Pb, Zn and Cd on the growth and metal uptake by investigating four aquatic plant species. **Azad et al (1984)** studied the heavy metal pollution caused by industrial units situated in the vicinity of Ludhiana (India) **fisher et al (1986)** studied effluent – toxicity due to trace metals near power plants. They noticed occurrence of certain trace elements in effluent of power plant. **Govardhan (1989)** studied heavy metal pollution of different inland lakes of Northern Himalaya. Inland lakes are vital resources to provide water food and recreation for human beings as well as many species of plants.

Hundal and Sandhu (1990) studied accumulation and distribution of various heavy metals in soils irrigated with sewage waste water irrigated mixed water irrigated and tube well water irrigated and analysed for total and DTPA extractable toxic Metal (Pb, Cd, Ni and Cr) contents. **Israeli (1991)** studied the occurrence of heavy metals in Ganga river water and sediments of various districts of Uttar Pradesh like Meerut **Goel (1992)** studied the distribution of heavy metals in soil and polluted river water in and around farm land before and after effluent discharge of an industrial unit of Yamunanagar (Haryana) India. **Gupta (1993)** estimated the concentration of six heavy metals viz. Manganese, iron, Nickel, Copper, chromium lead in Betwa river water form Nayapura to vidisha in year 1991. **Foy and Weil (1995)** observed that cotton genotypes shown previously to differ in tolerance to an acid (PH 5.1) Manganese Grenada Soil from Arkansas were grown in nutrient solutions containing variable concentration of excess Mn to confirm and characterize their postulated differences in Mn tolerance.

VIGNA RADIATA

Table and figure show the effects of pretreatment of seeds with various concentrations (0, 50 and 100 mg/1) of manganese on germination and subsequent seedling growth of Vigna radiata, linn, cultivars CT 163 in dark.

GERMINATION

Table indicates that lower concentration of Mn increases germination percentage where as higher Mn concentration inhibits germination percentage in dark in this cultivar. However the extent of inhibition is more in higher concentration.

Thus germination is inhibited by Ca 10% in 100 mg/1 concentration of Manganese

Table effect of manganese on germination percentage of Vigna radiata CVT 163 seedling grown in dark

Concentration of Manganese mg/1

Cultivar	0	10	50	100
T-163	95.00	93.00	90.35	86.40

Seedling growth : Table and figure show that like germination seedling growth is also promoted in lower concentration of Mn and inhibited in higher concentration in dark in this cultivar. However, growth is promoted in 10 mg/1 Mn concentration in dark. Thus in 10 mg/1 Mn concentration the length of epicotyl in dark is 128.8% 14.5% and 132.8% of control respectively on 3rd, 5th and 7th day of germination. Similarly the length of radicle in the 10 mg/1 Mn concentration in dark is 129.8% 137.4% and 125.4% of control respectively on 3rd, 5th and 7th day of germination, likewise, in this CV. in dark the fresh weight of epicotyl in 10mg/1 Mn concentration is 123.0%, 129.1%, 111.6% of control respectively on 3rd, 5th and 7th day of germination. Similarly results are also observed with radicle fresh weight. Beyond 50mg/1 Mn concentration the inhibition of seedling growth is observed. At 50mg/1 Mn and 100mg/1 Mn concentration the pattern of inhibition is nearly same in radicle and epicotyl in both the conditions. Thus in 100mg/1 Mn concentration the length of radicle in dark is inhibited by Ca 40%, 30% and 29% respectively on 3rd, 5th and 7th day of germination. Similarly, epicotyl fresh weight inhibition also found in this cultivars in 100mg/1 Mn concentration under similar conditions nearly similar pattern of inhibition is observed in this cultivar at 50mg/1 manganese concentration. Thus in this species organ specific differences in response to heavy metal manganese exist.

Table also indicate dry matter transfer in presence of dark as affected by different concentrations of Mn. Results show that dry weight of seedling parts is increased from 3rd to 7th day of germination. This increase is found to be paralleled by decrease in dry weight of cotyledon further, retention of dry matter in cotyledon gradually increases with increase in Mn.

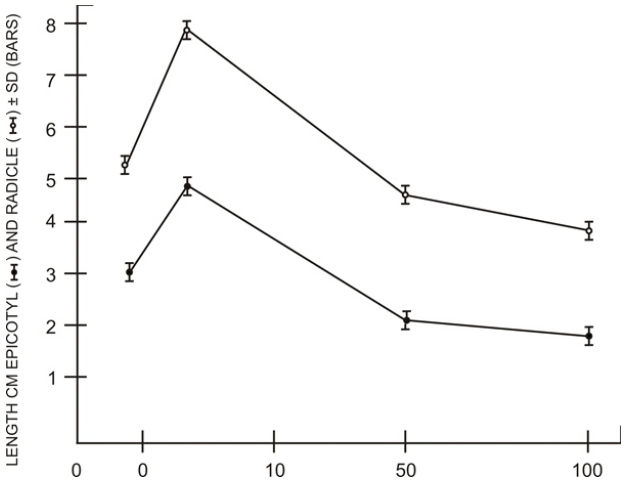


Figure: Dose response curve of 5 day old seedlings of Vigna radiata CV. T 163 in different concentrations of manganese

Table effect of 24 hours pretreatment of seeds with different concentrations of manganese on the seedling growth of Vigna radiata CV. T163 in Dark

Mn concentration Mg1-1	Length	CM±SD	Days After Radicle	Fresh emergence	Weight	Mg±SD
	3	5	7	3	5	7
0	4.63± 0.35	5.45± 0.28	6.87± 0.27	70.30± 4.68	81.59± 5.36	110.90 ± 8.78
10	6.01± 0.43	7.49± 0.36	8.62± 0.54	86.53± 5.70	105.38 ± 8.37	123.80 ± 9.61
50	4.10± 0.32	4.88± 0.39	5.90± 0.37	61.55± 4.31	72.54± 5.18	96.43 ± 5.72
76100	2.80± 0.18	3.81± 0.35	4.80± 0.31	38.73± 3.19	51.33± 4.14	66.79 ± 4.68

Epicotyl						
0	2.25± 0.27	3.32± 0.30	6.49± 0.31	53.75± 4.20	94.16± 8.32	146.30 ± 11.46
10	2.90± 0.23	4.70± 0.38	8.62± 0.41	71.26± 4.74	113.45 ± 7.30	175.15 ± 10.13
50	1.93± 0.15	2.83± 0.32	5.15± 0.31	65.14± 3.46	80.37± 6.92	93.14 ± 8.46
100	1.60± 0.10	2.05± 0.28	3.50± 0.17	42.50± 4.31	73.56± 5.48	81.40 ± 6.38

REFERENCES

1. Adam, F. and J.I. Wear (1957): Manganese toxicity and soil acidity in relation to esikle leg of cotton, Soil Sci, Soc. Amr, Proc. 2. 307-80.
2. Agarwal, S.K. (1989) studies on certain physiological effects of lead pollution, Ph.D. thesis Meerut University Meerut (India).
3. Azad, A.S. B.R. Arora B. Singh and G.S. Sekhon (1984) Nature and extent of heavy metal pollution from industrial units in Ludhiana (Punjab) Ind. J. Ecol. 11 (1): 1-5
4. Bhargava, T.N. (1996) uptake of heavy metals by some crop plant parts from solutions and polluted river waters. Ph.D. thesis C.C.S. University Meerut U.P. India.
5. Brown J.C. (1977) Manganese and Iron toxicities dependant on Soyabean variety Soil. Sc. and Plant Analysis 8:1-15.
6. Elomin O.M. and G.E. Willex (1986) Manganese toxicity development in Muskmelon Journ. Ann. Soc. Hort. Sci. 3:582-87.
7. Foy, C.D. R.R. Sweil (1995) Differential Manganese tolerance of cotton genotypes in nutrient solution Journ. of plant nutrition 18 (4) : 685-706.
8. Goel, J.P. (1992) studies on the effects of polluted water on certain crops with particular reference to distillery-effluent discharge Ph.D. thesis Meerut University, Meerut (India).
9. Govardhan V. (1989) heavy metal pollution of different land lakes of Northern –Himalayas Ind. Journ. Environ. Projection 9 (7) 531-36.
10. Gupta, S.K. R. Shukla, A. Agarwal and K.C. Gupta (1993) Estimation of toxic metals in river Betwa at Nayapura district- Raisen M. P (India) Sympos. on Environ. Degradation and Society Yamuna nagar Haryana (India)
11. Hundal, K.S. and S.S. Sandhu (1990) Movement of heavy metals in flowing sewage waste water an sludge Indian J. Environment prot. 10 (3)
12. Israeli, A.W. (1991) occurrence of heavy metals in Ganga river water and sediments of western Uttar Pradesh Pollution Research 10 (2) : 103-105.
13. Kozak, L. and C. Tarkowski (1979) Manganese copper iron magnesium and zinc contents and different growth and ages of triticale wheat and Rye Rogz Nauk Zootect 104 (2) 113-16.
14. Lohnis, M.P. (1951) Manganese toxicity in field and market garden crops. Plant and Soil 3 (3) : 193-222
15. Say, P.J., J.P.C. Harding and B.A. Whitton (1981) Aquatic mosses and monitors of heavy metal contamination in the River Etherow, Great Britain, U.K. Environ. Pollut. Ser. Bio Chem. Phys. 2 (4) 295-308.
16. Sharma, S.S. (1982 a) : Effects of mercury on germination and seedling growth of different varieties of Phaseolus aureus Ind. 3 Ecol. 9 (1) : 7
17. Souto, S.M. and J. Doberneiner (1971) Manganese toxicity in tropical forage legumes Pesqui Agrofeecu Bras 4 128-38.
18. Strong, J.D. Joy and L. Sistrunk (1985) Manganese toxicity shows up as brown speaks on firn leaves Pecon Suth Incl. 19 : 32-33.
19. Traverse, R.J. and C. Rickless (1973): Manganese enrichment on tomacco and onion seeds Journ amm. Hort. Soc. 18 : 120-23.
20. Vander Werff. Madeliin and M.J. Pruyt (1982) long term effects of heavy metals on aquatic plants chemosphere 11 (8) : 727-740.
21. Vlamis, J. and D.E. Williams (1973) Manganese toxicity and Marginal Chlorosin of lettuce Plant and Soil 39 : 245-51

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SYNTHESIS AND ANTIFUNGAL EVALUATION OF COMPLEXES OF TRANSITION METAL IONS (COPPER) WITH MIXED LIGAND DIBASIC TRIDENTATE SCHIFF BASES AND NAPHTHOIC ACID

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ABSTRACT

The present work deals with the synthesis of mixed ligand complexes of Cu(II) with dibasic tridentate Schiff bases derived by the condensation of thiosemicarbazides with acetoacetanilide and o-chloro- acetoacetanilide as primary and 1-hydroxy-2-naphthoic and 3-hydroxy-2-naphthoic as co-ligand.. The complexes were characterized on the basis of their elemental analysis, magnetic, spectral and electrolytic conductance study. Different ligand field parameters were also calculated. Cu (II) complexes and ligand were also screened for their antifungal activity against different fungi strains viz- ***Drechlera tetramera, Alternaria alter*nate and *Fusarium oxysporum*.**

Keywords: Tridentate Schiff base, Mixed ligand, Naphthoic acid, Antifungal activity, Copper complexes

INTRODUCTION

The coordination chemistry of transition metals and their derivatives has gained much importance in the recent years mainly because of their biological significance. The transition metal complexes of a Schiff bases have been widely researched on account of their value as biochemical, analytical and antimicrobial reagent. The metal thiosemicarbazone compounds are emerging as a new class of experimental anticancer chemotherapeutic agents. Semicarbazones and thiosemicarbazones are amongst the most widely studied nitrogen and oxygen and sulphur donor ligands.The transition metal complexes of Cu(II) with dibasic tridentate Schiff bases derived by condensation of thiosemicarbazide with acetoacetanilide as primary ligand and 1-hydroxy-2-naphthoic acid as co-ligand. The mixed ligand complexes of the above mentioned metal ions were characterized by analytical, magnetic and electronic spectral study. Copper (II) complex: The curpric ion has $3d^9$ configuration having one unpaired electron. Its complexes usually have square planar to tetragonal distorted octahedral stereochemistry. However, irrespective of the stereochemistry involved, the magnetic moment has been found to be (with spin-orbit coupling constant of 850 cm^{-1}) about 1.92 B.M. The transition metal complexes were also evaluated for antifungal activity against Drechslera tetramera, Fusarium oxysporum and Aternaria alternata

at different concentrations. The study confirmed that Cu(II) is the most active fungicide.

Transition metal complexes of Schiff bases have been amongst the most widely studied coordination compounds in the last few years, because of their importance as biochemical, analytical and antimicrobial reagents[1-3]. Metal complexes formed by ligands which are capable of coordinating with two or more sites with metal ions have evoked much interest in the field of coordination chemistry[4-6]. The Schiff bases derived from a large number of carbonyl compounds and amines have been reported and they are found to form complexes with metal ions. The metal complexes formed by ligand 2-amino-4-phenyl-5-arylazothiazole and salicylaldehyde have been reported in literature[7,8].

Nitrogen, oxygen and sulphur donor ligands possess a large range of biological applications like antitumour [9], antiviral[10], antibacterial[11], antimalarial[12], and antifungal activities[13]. Manganese ethylene bisdithiocarbamate is known to show antifungal activity and are used against a variety of diseases[14], specially of vegetables and fruits[15]. Manganese complexes of some thiosemicarbazones are potent antileukemic agents[16]. Recently metal thiosemicarbazone compounds emerged a new class of experimental anticancer chemotherapeutic agents[17] which show inhibitory activity against most of the cancers through inhibition of a crucial enzyme obligatory for DNA biosynthesis and cell division[18,19].

The survey of the literature revealed that mixed ligand complexes of transition metal ions with dibasic tridentate Schiff bases derived by the condensation of thiosemicarbazides with o-Chloro-acetoacetanilide as primary and 1-Hydroxy-2-naphthoic acid and 3-hydroxy-2-naphthoic acid as co-ligands have not been studied so far. The present work deals with the preparation and characterization of mixed ligand complexes of few transition metal ions with primary and secondary ligands. The newly prepared mixed ligand complexes were characterized on the basis of their elemental analysis, magnetic, spectral and electrolytic conductance studies. These mixed ligands complexes were also screened for their fungicidal and antimicrobial studies.

EXPERIMENTAL

Cu(II), thiosemicarbazide, acetoacetanilide, O chloroacetoanilide, hydroxyl-2-naphthoic acid and 3-hydroxy-2 -naphthoic acid, dimethyl formamiode (DMF) and alcoholic were purchased from fischer scientific, India. All the reagents used were of chemically pure or analytical reagent grade. Solvents were purified and dried before use.The analysis was performed at CDRI's Lucknow, India. Conductance of the metal complexes were measured in nitromethane at 25°C on Toshniwal conductivity bridge CL01/01 usind dip type cell.The following accepted range of molar conductivity for water at concentration equal to M/1000 and temperature 25°C were taken to determine the number of ions present in solution. The standard range of molar conductivity in mhos of uni-divalent electrolyte is 215-273 mhos

Infrared spectra of the ligand and Cu (II) complexes were recorded on Beckmann IR 120 Spectrophotometer and Perkin Elmer improved 137 spectrophotometer in Nujol mull and KBr in the range 200 to 400 cm^{-1} and 400-4000 cm^{-1} at room temperature. The electronic spectra of the complexes were recorded in ethanol at room temperature on CZ-specord UV-vis-spectrophotometer provided with an automatic recorder. The magnetic susceptibility at room temperature was determined on Gouy's electromagnetic balance and corrected for dimagnetism.

PREPARATION OF PRIMARY LIGAND : (DIBASIC TRIDENTATE SCHIFF BASES)

The primary ligand (Schiff base) was prepared by refluxing thiosemicarbazides with o-chloro-acetoacetanilide in 1:1 molar ratio in alcohol for an hour on water bath. After refluxing it was concentrated on water bath to half its volume. The precipitate obtained after condensation was filtered and dried. The formation of ligand was confirmed by its elemental analysis and I.R. studies.

PREPARATION OF MIXED LIGAND COMPLEXES

To a warm ethanolic solution of anhydrous metal chlorides or acetates, hot ethanolic solution of Schiff base i.e. Primary ligand was added drop wise. The reaction mixture was thoroughly stirred and refluxed on water bath for three hours. Crystalline complexes formed with primary ligand separate out on cooling at room temperature. The complexes were filtered off, washed with ethanol and finally with ether to remove the excess of ligand and then dried in vacuums.

The mixed ligand complexes were prepared by treating the ethanolic solution of binary complexes with ethanolic solution of 1-hydroxy-2-naphthoic acid or 3-hydroxy-2-naphthoic acid. The reaction mixture was refluxed on water bath for about four hours in each case. The reaction mixture was kept overnight at room temperature. The complexes formed in the form of precipitate were filtered, washed with acetonitrile and finally with ether to remove unreacted ligand if any.The mixed ligand complexes were dried in vacuum yield 80%.

RESULT AND DISCUSSION

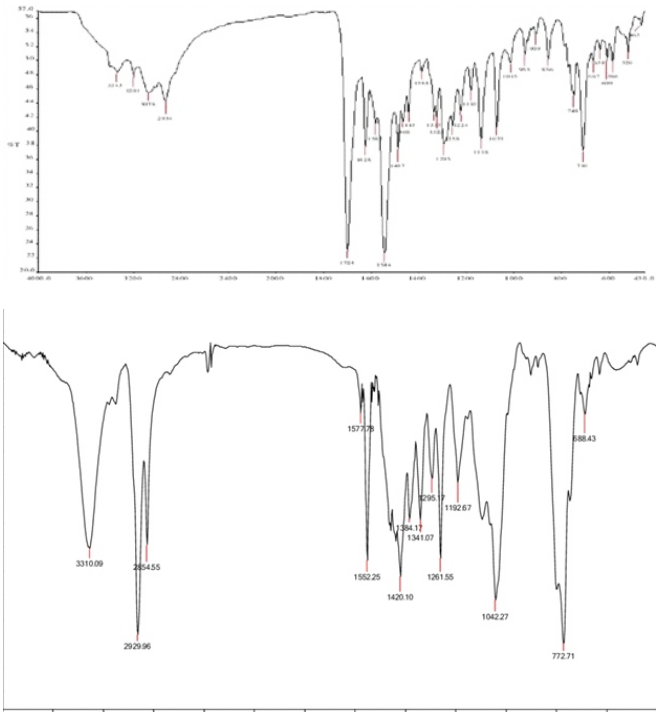
Analytical data of mixed ligand complexes shows 1:1:1 (M:L:L':L") stoichiometry of isolated mixed ligand complexes (where M=Cu(II), L=$C_{11}H_{13}N_4SOCl$, L'=$C_{11}H_8O_3$, L"$C_{11}H_8O_3$). All the complexes were stable upto 150°C indicating that they are non-hygroscopic.All the mixed ligand complexes are soluble in common organic solvents.The conductance data shows that they are having non-electrolytic nature.

I.R. STUDIES

On comparison of I.R. spectra of free ligand, with those of the mixed ligand complexes confirm the coordination of thiosemicarbazone and naphthoic acid to the metals. I.R. spectra of free thiosemicarbazone ligand (Schiff base) show two band at 3440 and 3320 cm^{-1} due to V_{as} and V_{sym} of terminal NH_2 group. In complexes these bands were found unchanged showing the non-involvement of this group in coordination. The absorption due to nC=N of the free ligand appear in the region 1610 cm^{-1} undergoes a negative shift by 10-15 cm-1 in the spectra of complexes indicating the coordination of azomethine nitrogen to the metal.

The bands of strong intensities in the spectra of the Schiff base around 1645 cm-1 are due to nC=0. In the spectra of complexes, this band is absent and a new band is observed at 1615 cm^{-1} which can be attributed to the enolisation and subsequent coordination through the deprotonated oxygen atom of the —CH_2—C=0 group. The band due to nC=S appearing at 820 cm-1 in the free Schiff base disappear on complexation and a new band appears around 745 cm^{-1}. These observations may be attributed to the enolisation of the —NH—C=S group and subsequent coordination through the deprotonated sulphur. From I.R. data it may be inferred that the thiosemicarbazone is potentially dibasic tridentate ligand and the coordination sites are the α-nitrogen and thiolato sulphur and oxygen after deprotonation. The possibility of a-Nitrogen coordination is ruled out because of considerable strain.

The nOH (of COOH group) observed as a broad intense band at 2645 cm-1 in naphthoic acid has no change in the spectra of the mixed ligand complexes, indicating that the carboxylic photon has not been removed in complexation. The symmetrical and asymmetrical stretching vibration of -COO of free ligand observed at 1410 and 1630 cm^{-1} respectively has shifted to 10-15 cm-1 in the complexes indicating coordination of carboxylate oxygen to metal ion. The band observed at 2965 assigned to phenolic-OH of acid also get shifted indicating that-OH is coordinated to metal. This is also confirmed by the observation of M-O band in the spectra.



MAGNETIC AND ELECTRONIC SPECTRAL STUDIES

Correlations of the magnetic and spectral properties of transition metal complexes derived from nitrogen, sulphur and oxygen donor atom ligands have been reported recently by number of chemists.

CU (II) COMPLEXES

The cupric ion has $3d^9$ configuration having one unpaired electron. Its complexes usually have simple square planar to tetragonally distorted octahedral stereochemistry. However, irrespective of the stereochemistry involved the magnetic moment has been found to be (with spin-orbit coupling constant of 850 cm-1) about 1.90 B.M. Generally octahedral coordinated Cu(II) complexes have magnetic moment in the range of 1.90-2.20 B.M. and the values are independent of temperature. But Figgis predicted a magnetic moment >1.90 B.M. for tetrahedral and <1.90 B.M. for square planar and octahedral Cu(II) complexes. The square planar complexes of Cu(II) ion may rightly be called as extreme cases of tetragonally distorted, Octahedral geometry around the central metal ion and in such environment the separation between the ground level $^2B_{1g}$ and the components of $^2T_{2g}$ term of the Cu (II) ion is larger than in octahedral complexes. Which possibly seems to be responsible for the lower magnetic moment values of square planar complexes? However no significant conclusion concerning the stereochemistry of Cu (II) compounds can be drawn nearly on the basis of magnetic data. The present Cu(II) complexes are paramagnetic exhibiting magnetic moment in the range 1.84-1.88 B.M. normally accepted for. The electronic spectra of Cu(II) complexes shows only one absorption band around 16000 cm-1 which may be assigned to the transition 3Eg $2T_{2g}$ characteristic of distorted octahedral Cu(II) complexes distorted octahedral stereochemistry.

ANTIFUNGAL AND ANTIBACTERIAL ACTIVITIES

The data for the antifungal and antibacterial activities of the ligands and their complexes against various fungi and bacteria have been recorded. The results point out that the complexes are inhibiting the growth of fungi and bacteria to a greater extent as the

concentration is increased. The enhanced activity of mixed ligand complexes may be ascribed due to increased lipophilic nature of these complexes arising due to chelating. It is also noted that sulphur containing ligands as well as their complexes are more active that their oxygen containing counterparts. The toxicity increases as the concentration is increased. Mode of action of antimicrobials may involve various targets in microorganism of interference with the cell wall, synthesis, damage to the cytoplasmic membrane as a result of which cell permeability may be altered or they may disorganize the lipoprotein leading to the cell death.

TABLE: 1 FUNGICIDAL TESTING OF LIGAND (PRIMARY+SECONDARY) AND ITS METAL COMPLEXES

Growth responses of drechslera tetramera, alternaria alternata and fusarium oxysporum (after 96 hours at 26+1o on czpeck's dox agar medium) at different concentrations (in ppm) in relation to the ligand and its metal complexes

Test Sample	Average % inhibition after 96 hours								
	Drechslera tetramera			Alternaria alternata			Fusarium oxysporum		
	Concentration used in ppm								
	500	200	100	500	200	100	500	200	100
Ligand (Primary + Secondary)	70.0	50.1	30.4	68.8	49.8	28.9	69.4	48.8	30.2
Cu Complex	52.2	36.8	21.7	53.0	36.6	22.8	52.5	35.0	22.3

CONCLUSION

The work concludes with the synthesis of the ligands benzofuro-2-carboxy-phenyl thiosemicarbazide and benzofuro-2-carboxy-[4'-chlorophenyl] thiosemicarbazide. Further metal complexes of Co(II) mono-nitrophenates. The structure of newly synthesized complexes and the ligands were established with UV-visible spectroscopy, infrared spectroscopy and magnetic studies. The magnetic moment value of Cu(II), complexes suggested distorted octahedral and octahedral geometry. From the fungicidal activity data, it is evident that among all the metal complexes tested for their antifungal activity, Cu(II) complexes are most active fungicides. The fungicidal action of Cu(II) complexes may be explained due to inactivation of enzymes. The other metal complexes are however not much fungi toxic for the particular fungi. Generally, the fungi toxicity enhanced with increase in the dose of complex.

REFERENCES

1. Johnson D.K., Murphy T.B., Rose N.J. and Goodwin W.H., Inorg. Chem. Acta, **67** (1982) 159.
2. Elshahawi M.S., Anal. Sci., **7**(1991) 443.
3. Mishra A.P., Srivastava S.K. & Srivastava V., J. Indian Chem. Soc.**73** (1996) 261.
4. Chakrabarti J and Sahoo B., Indian J. Chem. 20A (1981) 931.
5. Deshpande U.G. and shah J.R., J. Macromol Sci Chem., **20**(3) (1983) 355.
6. Patel K.M., Patel N.H., Patel K.N. and Patel M.N., Synth. React. Inorg. Met. Org. Chem., **30** (2000) 1953.
7. Sharma C.L., Mishra V and Narvi S.S., Synth. React. Inorg. Met. Org. Chem. **16**(1986) 243.
8. Sinha C, Trans. Met. Chem. **19** (1994) 14.
9. Gupta S.K.S., Pandey O.P. and Bhatt A., Srivastava V. and Mishra K.N., Indian J. Chem., **41A** (2002) 1421.
10. Ibrahim K.M., Mostafa S.I., Nawar N. and Younis Z.A., Indian J. Chem., **43A** (2004) 2294.
11. Maurya R.C., Pandey A and Sutradhan D, Indian J. Chem. **43A** (2004) 763.
12. Dave S., Chaudhary A., Agrawal M. Joshi S.C. and Singh R.V., Indian J. Chem. **42A** (12003) 268.
13. Dey K., Bikash B and Sarkar S., Indian J. Chem. **43A** (2004) 773.
14. Mishra R. Sharma K. and Singh R.V., Oriental J. Chem. **18(1)** (2002) 85.
15. Kasuga N.C., Sekino K, Ishikawa M. Hinda A., Yokoyama M., Nakano S., Shimada N. Koumo C. and Nomiyak, J. Inorg. Biochem., **96** (2003) 298.
16. Patel I.A., Patel P., Goldsmiths and Thakar B.T. Indian J. Chem., **42A** (2003) 2487.
17. Patole J., Padhye S., Padhye S., Newton C.J., Anson C and Powell A.K. Indian J. Chem. **43A** (2004) 1654.
18. Munugkar A. Unnikrishan B., Padhye S.B., Bhonde R. Teat S. Triantafillan E and Sunn E., Metal Based Drugs **6**(1999) 177.
19. Murughar A., Padhye S.B., Gaha Roy S and Wagh 4., Inorg. Chem. Commun.**2** (1999) 545.

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STUDY ON THE CHARACTERIZATION OF TRANSITION METAL COMPLEXES AND THEIR ANTIBACTERIAL PROPERTIES

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ABSTRACT

This study reviews on the Macrocyclic ligands that are polydentate ligands that contain donor atoms either incorporated or linked to the cyclic backbone and have been shown to have biological importance in a variety of investigations. Using the template technique, tetraaza macrocyclic complexes of transition metals Ni(II), Cu(II), Fe(III), and Mn(II) were produced in methanolic conditions. These complexes lacked hygroscopicity and were composed entirely of crystalline solids. The structures of these complexes were determined using the analytical methods UV-Vis and IR Spectroscopy. Antibacterial activity of macrocyclic complexes (1-6) was evaluated against Gram-negative (Escherichia coli and Vibrio cholerae) and Gram-positive microorganisms (Bacillus subtilis and Staphylococcus aureus). We observed in this work that these manufactured complexes had only a weak antibacterial activity, with the exception of macrocyclic complex (6), which exhibited moderate antibacterial activity.

Keywords: Transition Metals, Macrocyclic Complexes, UV-Vis and IR Spectroscopy.

INTRODUCTION

There has been a lot of interest in macrocyclic complexes recently because of their connection to biomimetic and catalytic systems, as well as their potential utility in medicine and chemistry [M.P. Reddy et al., 2012; D. E. Fenton and H. Okawa, 1993]. Macrocyclic complexes are becoming increasingly important. However, inorganic chemists throughout the globe are interested in the coordination chemistry of macrocyclic complexes [S. Chandra et al., 2009]. They are extremely useful as pigments and colourants due to their vivid hues and chemical inertness [S. Karaboceket al, 2006; K. Shankar et al, 2009]. There is a lot of interest in bioinorganic chemistry at the moment. The importance of macrocycles in biology has led to a new trend in the study of their complexation chemistry with a wide range of metal ions [D. Singh et al, 2010; S. Chandra et al, 2006].

Metalloporphyrin and metallocorrin structural features in macrocyclic complexes are analogous to those in synthetic models [E. Kubaszewski and T Malinski, 1992; R. Vaumet et al., 1982]. For the synthesis of more complex compounds with potential medical applications, new avenues of research such as those undertaken by J. Eilmes and colleagues (in 1985 and 1997) to achieve peripheral substitution that provides points of attachment for further structural modification are now open to us. When it comes to figuring out how macrocycles work in the body, studying synthetic model molecules like these can be helpful [S. Cunha et al., 2005].

As a result of macrocyclic complexes' many pharmacological and coordination features [E.V. Caemelbecke et al, 2005; E. Kimura, 1993], researchers have focused their efforts on them. antibiotics are utilised in both humans and animals as a significant therapeutic chemical to treat infections. [D. Guillemot, 1999; T. Rosuet al, 2006]. According to recent investigations, frequent use of antibiotics results in a growing therapeutic issue [R. Corrêaet al, 1998; G. Turhan-Zitouniet al, 2001]. Antibiotic resistance inhibitors in the form of macrocyclic complexes can assist to minimise this. While macrocyclic compounds and their antibacterial properties are of great relevance, this paper was taken into consideration. The basic objective of this research is to analyze the characterization of Transition Metal Complex.

All chemicals used in this study were of AnalaR Grade. Six macrocyclic complexes were synthesized and characterized.

Synthesis of Macrocyclic Complexes

All Complexes were produced utilising template approach by condensation of acefone/diacetyl in the presence of corresponding metals salts. To a methanolic solvent (=50), o-phenylenediamine/3, 5 diamino benzoic acid with acetone/diacetyl followed by metal salt in ratio 2:2:1 were added in round bottom flask. Shake thoroughly and refluxing was carried out for 6-8 hours. The change in colour was appeared. The circular bottom flask was placed aside for its chilling. The filtering and washing were carried out by methanol and dried in vacuum. The coloured compounds were obtained and taken for further investigations.

METHODOLOGY

Table 1 Analysis of Macrocyclic Complexes

Macrocyclic Complexes (Molecular Formula)	Color	Yield(%)	Elemental Analysis							
			C%		H%		N%		M%	
			Cal.	Found	Cal.	Found	Cal	Found	Cal	Found
MC-I/C H N Nicl O	Purple	45	43.72	42	4.3	4	9.27	9.1	13	12
MC-II/C H N CuCl O	Blue	40	41.4	41.2	3.54	3.5	8.05	8	11.1	11
MC-III/C H N CuCl O	Blue	44	41.37	40.2	3.78	3.75	9.35	9	9.35	9
MC-IV/C H N FeCl O	Green	50	52.42	51.5	4.46	4.4	10.8	9.5	10.8	10.35
MC-V/C H N FeCl O	Pale Green	42	70.98	70.8	4.22	4	9.02	7.75	9.02	8.9
MC-VI/C H N NiCl O	Violet	40	56.96	56	4.52	4.5	9.7	12.02	9.7	9.3

CHARACTERIZATION

Elements (C, H, and N) and colours and yields were analysed for all the complexes. A spectrophotometer was used for the UV-Vis measurements (Systronics UV-Vis spectrophotometer 117). There were 50 scans on the Nicolet Aligent 1100 FT-Ir spectrometer, and the results were published in infrared spectra. In IR spectra, a decrease in $\nu_{C=N}$ to 7–10 cm^{-1} relative to the free ligand was seen for all complexes containing azomethine nitrogen coordination.

BIOLOGICAL ACTIVITY

A variety of bacteria cultures, including Escherichia coli and Vibrio cholerae, Staphylococcus aureus and Bacillus subtilis, were used to test the antibacterial activity of the target compounds that were produced in this study. In this study, Escherichia coli and Vibrio cholerae, Staphylococcus aureus and Bacillus subtillus were isolated from the MTCC (Microbial Type Culture Collection), and used as test isolates. The preliminary antibacterial activity was determined using the

Agar-diffusion technique, which was previously described. A sterile disc of 5 mm diameter made of filter paper (Whatsmann no. 1) and impregnated with test macrocyclic complexes (10 mg/ml of DMSO) was used in this approach, and it was incubated at 37°C for 12 hours. After 12 hours, the inhibition zones around the dried impregnated discs were assessed using a scanning electron microscope. The Antibacterial activity was classed as extremely active (>14 mm), moderately active (10-14 mm), somewhat active (6-10 mm), and inactive (less than 5 mm). Less than 5 mm was considered inactive. By employing a micro broth dilution procedure, it was possible to calculate the minimum inhibitory concentration (MIC) of the substances. A standard culture of test bacteria was injected with varying doses of the chemicals using the broth dilution microbiological technique (MIC method). In the wake of an overnight incubation at 37 degrees Celsius, the minimal inhibitory concentration (MIC) of the compounds was calculated by monitoring the lowest concentration of the compounds that would suppress observable growth of the test bacteria. The optical density (OD) at 600 nm was used to measure growth, which was calculated photo metrically.

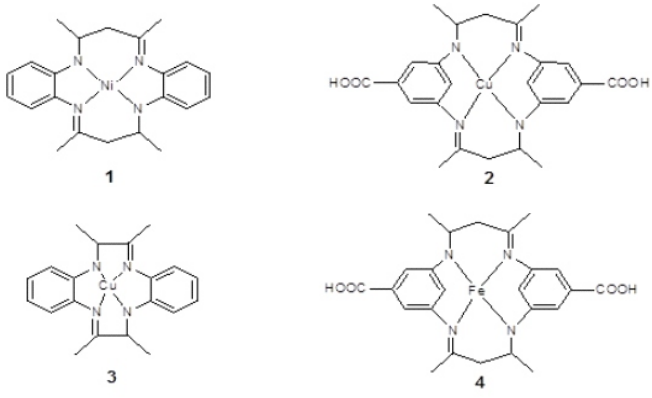
RESULTS AND DISCUSSION

The present studies described the six macrocyclic complexes (I-VI) of different metals synthesis and their antibacterial activities. These complexes were crystalline solids and non-hygroscopic. The formulae for these macroxyclic complexes were assigned on the basis of analytical data and enable us to predict the possible structure of the synthesized complexes.

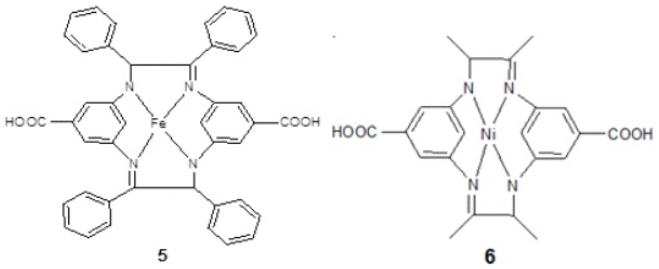
Table 2 UV-Vis Spectral data of Macrocyclic Complexes (nm)

Molecular Formula	λ max (nm)
$C_{22}H_{25}N_4NiCl_2O_8$	548.4
$C_{24}H_{25}N_4CuCl_2O_{12}$	402
$C_{20}H_{22}N_4CuCl_2O_8$	374
$C_{24}H_{25}N_4FeCl_2O_4$	520
$C_{42}H_{30}N_4FeCl_2O_4$	425
$C_{22}H_{21}N_4NiCl_2O_8$	389

Table 2 shows the electronic absorption spectrum data of the complexes in dimethyl sulfoxide (DMSO) at ambient temperature for the different compounds. When complexes are dissolved in DMSO, their electronic spectra exhibit bands in the visible–ultraviolet range. In the azomethine (-C=N) group of compounds, the absorption bands below 400 nm are almost similar and can be ascribed to ð-ð* transitions occurring in the C=N group. The Ni(II) complexes have a square-planar geometry around the central metal ions, whereas the Cu(II) complexes have an octahedral geometry around the core metal ions [S. Chandra and L.K. Gupta 2004; S. Chandra and S.D Sharma 2002]. The absorption bands found in the 350-550 nm region are most likely due to transitions of the n- π** of the imine group [E. Konig, 1971], with the transitions of the n- π* of the imine group being the most likely explanation. [B.N. Figgis and M.A. Hitchman, 2000; A.A.A. Emara and M.I.A. Omima, 2007] The electronic spectra of nickel(II) and its complexes exhibit an absorption band at 380-550 nm that has been attributed to the 2Eg 2T2g transition, which is characteristic of tetragonally elongated octahedral or square planar Ni(II) and Co(II) complexes have been demonstrated to have electronic absorption bands in the visible range that are dependent on the presence of a solvent.



1 2 3 4



5 6

Fig. 1 Proposed Structures of Dicataionic form of Macrocyclic Complexes, where 1-6 are macrocyclic complexes I-VI

These results are consistent with documented red shifts in the low energy d-d band of Ni (II) and Co(II) complexes in DMSO, which can be explained in part by the presence of a weak ligand field. The infrared spectra of KBr pellets were acquired on a Nicolet Nexus Aligent 1100 FT-IR spectrometer using 50 scans and were reported in centimetres per metre per second (cm^{-1}). For all complexes coordination of azomethine nitrogen was supported by lowering of $\nu_{C=N}$ to 7-10 cm^{-1} as compared to free ligand in IR spectra. Results of IR-spectroscopy were summarized in the table below:

Table 3 Infrared Spectral Data of Macrocyclic Complexes (cm^{-1})

Molecular Formula	ν(NH)	ν(ClO_4)
$C_{22}H_{26}N_4NiCl_2O_8$	3240s	1097(s,b) 623m
$C_{24}H_{25}N_4CuCl_2O_{12}$	3220s	1092 (s,b) 620m
$C_{20}H_{22}N_4CuCl_2O_8$	3210m	1090 (s,b) 618m
$C_{24}H_{25}N_4FeCl_2O_4$	3200s	1100 (ns,b) 620s
$C_{42}H_{30}N_4FeCl_2O_4$	3210s	110 (ns,b) 620s
$C_{22}H_{21}N_4NiCl_2O_8$	3230s	1080 (ns,b) 620s

Where s=strong, vs=very strong, b=broad, m= medium.

A band at 623 cm–1 in the infrared spectrum of Complex I indicated the presence of a noncoordinated perchlorate ion with a wavelength of about 1097 cm–1. It was discovered that complex II exhibited IR bands near 1092 cm-1, which, together with a band at 620 cm-1, indicated the presence of noncoordinated perchlorate ion, while complex III exhibited IR bands near 1090 cm-1, which, together with a band at 618 cm-1, indicated the presence of noncoordinated perchlorate ion. A series of very strong IR bands about 1100 cm-1, as well as a band at 620 cm-1, were seen in Complex IV, indicating the existence of non-coordinated perchlorate ion (Table 3). There were two extremely strong IR bands in Complex V, one around 1100 cm-1 and the other at 620 cm–1, which indicated that the perchlorate ion was present but not coordinated. Complicated VI had IR bands at 1080 cm-1 and a band near 600 cm-1, both of which indicated the existence of non-coordinated perchlorate ion in the sample. The macrocyclic complexes that have been proposed are (1) 1,4,8,11 dibenzotetraaza-tetradeca 7,14-Diene; (2) 1,4,8,11 dibenzotetraaza-tetradeca 7,14-Diene; and (3) 1,4,8,11 dibenzotetraaza-tetradeca 7,14-Diene. (2) 1,5,9,13-tetraaza dibenzoichexadeca 8,16 Cu(II) Macrocyclic complex, (3) 1,4,7,10-tetraaza dibenzododeca 6,12 diene Cu(II) Macrocyclic complex, (4) 1,5,9,13-tetraaza dibenzoichexadeca 8,16 diene Fe(III) Macrocyclic complex, (5) 1,5,8,12 tetraazad Iron III macrocyclic compound, (6) 1, 5, 8, 12, tetraaza dibenzoic acid 6,7,13,14 tetramethyl tetradeca 7,14-diene is a tetramethyl tetradeca 7,14-diene with the formula 6,7,13,14 tetramethyl tetradeca Ni(II) Macrocyclic Complex was discovered, and the related molecular structures were shown in figure 1.

CONCLUSION

The research described above was a previous examination of the antibacterial activity of macrocyclic complexes. It also demonstrates that the complexes have the power of generating novel antimicrobial metabolites when exposed to bacteria. The development of new chemical classes of antibiotics is the outcome of macrocyclic complexes demonstrating antibacterial activity; these complexes have the potential to be used as selective agents for the maintenance of human or animal health in the

future, as well as biochemical tools for the study of infectious disease.

REFERENCES

1. M.P. Reddy, R. Rondla, R.K. Edulla, H. Anren, R. Vadde, (2012). Synthesis, spectral and antibacterial studies of Copper(II) tetraazamacrocyclic complexes, International Journal of Molecular Sciences., 13 (4), 4982-4992.
2. D.E. Fenton, H. Okawa, (1993). Metal ion controlled synthesis of 16 and 18 membered by nuclear octaazamacrocyclic complexes with Co(II), Ni (II),Cu(II) and Zn(II): A comparative spectroscopic approach to DNA binding to Cu(II) complexes, Perspectives on Bioinorganic Chemistry, JAI Press: London, 8.
3. S. Chandra, D. Jain, A. Kumar, P. Sharma, (2009). Coordination Modes of a Schiff Base Pentadentate Derivative of 4- Aminoantiphyrine with Co(II),Ni(II) and Cu(II) Metal ions : Synthesis, Spectroscopic and Antimicrobial Studies, Molecules, 2009, 14, 174-190.
4. S. Karabocek, N. Karabocek, A. Armutcu, (2006). Synthesis and structural studies of 2-(hydroxyimino)-1-methylpropylideneamino-phennyiminobutan-2-one oxime, ligand and its complexes with CuII and NiII, Transition Metal Chemistry, 31, 459-464.
5. K. Shankar, M. Ashok, P.M. Reddy, R. Rohini, V. Ravinder, (2009). Spectroscopic characterization and antibacterial activities of Mn(III) complexes containing the tetradentateaza Schiff base ligands, International Journal of ChemTech Research, 1, 777-783.
6. D. Singh, K. Kumar, R. Kumar, J. Singh, (2010). Template synthesis and characterization of biologically active transition metal complexes comprising 14-membered tetraazamacrocyclic ligand, Journal of the Serbian Chemical Society, 75(2), 217-228.
7. S. Chandra, R. Gupta, N. Gupta, S.S. Bawa, (2006). Biologically relevant macrocyclic complexes of Copper.Spectral, Magnetic, Thermal and antibacterial Approach, Transition Metal Chemistry, 31, 147.
8. E. Kubaszewski, T. Malinski, (1992). 5,7,12,14-Tetramethyldimethoxybenzo [6,1][1,4,8,11] tetraazacyclodecane, a new tumoricidal pseudo-porphyrin, Journal of hetrocyclic Chemistry, 29 (6), 1417-1422.
9. R. Vaum, N.D. Heindel, H.D. Burns, J. Emrich, (1982). Synthesis and evaluation of Fe(III) In-labeled porphyrin for lymph no deimaging, Journal of Pharmaceutical Science, 1982, 71, 1223-1226.
10. J. Eilmes, (1985). Benzoylation of macrocyclic Ni (II) complex efficiently and year demetalation of Y-Y' -dibenzoylated products, Polyhedron, 1985, 4 (6), 943-946.
11. S.A.J. Collen, F.M. Everaerts, F.A. Huf, (1997). Characterization of 60Co Y-Radiation Induced Radical Products of Antipyrin by Means of HPLC, Mass Spectrometry, Capillary zone, Electrophoresis, Miceller Electro kinetic Capillary Chromatography and NMR Spectrometery, Journal of Chromatography A, 1997, 788, 95-103.
12. S. Cunha, S.M. Oliveira, Jr M.T. Rodrigues, R.M. Bastos, J. Ferrari, C.M.A. De Oliveira, L. Kato, H.B. Napolitano, I. Vencato, C. Lariucci, (2005). Structural Studies of 4- Aminoantipyrine Derivatives, Journal of Molecular Structure, 752, 32-39.

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MACROCYCLIC METAL CHELATES OF DIVALENT IRON, COBALT AND NICKEL DERIVED FROM DIHYDRAZONE AND DICARBONYL COMPOUNDS

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ABSTRACT

Diacetyldilydrazone and 2,6-diacetylpyridine react in presence of divalent iron, cobalt and nickel salts to from chelates of 22 membered N_6, hexadentatemacrocycle. Chelates are characterized as distorted octahedral of the type $[M(C_{26}H_{30}N_{10})]\ X_2$ where M = Fe (II). Co (II) NI (II) and X = Cl, Br, NO_3 or NCS. The macrocycle coordinate through azomethine and pyridine nitrogen atoms which are bridged by diacetyl moieties. The chelates are characterized by electrical conductance, molecular weight, electronic and infrared spectral studies.

Keywords: Metal template effect, N_6macrocyclic chelates, Diacetyldihydrazone, Azomethine coordination, Py-N chelation

INTRODUCTION

Major part of the macrocyclic ligands have been synthesized by the condensation of amines with dicarbonyl compounds[1,2]. However, very few have been prepared form aromatic dicarbonyl and aliphatic dihydrazone compounds[3] and their structures have been established by X-ray crystallography[4,7]. In continuation of our studies on macrocyclic ligands[8,10], in present article we report the synthesis and characterization of six coordinate octahedral chelates of hexadentate N_6macrocycle. Attempts to isolate the free ligand failed.

EXPERIMENTAL

All the chemicals and reagents used were of reagent grade and were used as received. The diacetyl was procured from Reidel (W. Germany), 2, 6-diacetylpyridine from Aldrich Chemical Co. U.S.A. and hydrazinehydrate from BDH (UK).

synthesis of diacetyldihydrazone

It is synthesized by adopting the method prod by Bush and Bailar[13]. 5.0 ml (0.1 mole) of hydrazinehydrate was dissolved in 100ml of ethanol and 8.6 ml (0.1 mole) of diacetyl was added slowly in boiling condition.

Reflux the contents for about half an hour, ethanol was removed by dry distillation and resulted content cooled in ice bath. White crystals formed were washed with little water. Recrystallization was carried out by absolute alcohol and dried in vacuo. M.P. 160°, yield ~30%.

Synthesis and isolation of chelates

100 ml of methanolic solution of 3.0 gm (0.02m mole) 2,6-diacetyl pyridine and 2.2 gm. (0.02 mole) diacetyldihdrazone was mixed and reflux for an hour. Divalent iron, cobalt or nickel salt (0.01 mole) dissolved in minimum quantity (100ml) of methanol was added to the mixture and refluxing continued for six hours

on water bath. The metal template synthesis has been found to the condensation reaction resulting in the ring closure[14]. The use of metal as templating agent has led to the synthesis of many metal complexes of macrocylic ligands[15].

Different coloured solutions were concentrated to half of their volume and kept in desiccator for three days. The dark green or brownish- black crystals separated, were filtered off, washed with acetone, benzene, ether and dried in vacuo, yield - 60%.

RESULTS AND DISCUSSION

The analytical data given in Table-1, show that they may be represented as [M (C_{26} H_{30} N_{10})] X_2, where M=Fe (II), Co (II) or Ni (II) and X=Cl, Br, NO_3 of NCS. The chelates are soluble in water, methanol and DMF and are thermally stable upto 280°. The molar conductance of all the chelates measured in DMF and exhibit that they are 1:2 electrolyte. The test of anions are positive directly without decomposing the chelates, indicating their presence out side the coordination sphere.

Infrared Spectra

The IR spectra of all the chelates does not show any band in the region ~ 3200-3400 cm and ~1700 cm^{-1}, the characteristic frequency of free NH, and free carbonyl group, respectively. It indicate the absence 16, 17 of these groups in complexes. However, the strong bands appearing as doublets ~ 1595-1629 cm^{-1} may be assigned to v (C=N) vibrations show the coordinated azomethine group[16,18]. Therefore, spectra clears that both the NH_2 group of diacetyldihydrazone have condensed with both the carbonyl groups of 2,6-diacetylpyridine to give rise N_4 arrangement of azomethine nitrogen atoms equally suitable for coordination[19]. This content further supported[18] by appearance of various bands at ~ 2925, 1360, 1275 and 675 cm^{-1}assignable to v (CH_3),v (C=CH3), äsym v (CH3) and ring deformation modes and diacetyl moiety, respectively. The spectra also exhibit downward shift in the region ~ 1590-1610, 1570-1585, 1450-1490 and 1435-1440 cm^{-1}, which are assigned to four (C=C) and (C=N) skeleton frequencies of pyridine ring. Also, the bond assigned to Ö (C-C) splits into two ~ 720 and 740 cm^{-1} while (C-H) appears -785 cm^{-1} as a single band. These changes points toward the coordination of pyridine nitrogen atom[20,21].

The spectra do not show any band assigned to symmetric and antisymmetric N-H vibrations at ~3300 and 3110 cm which show the absence of NH group[22]. While appearance of band at ~990-1010 cm^{-1}, may be signed to (N-N) vibrations of dihydrazone. The 15-20 cm^{-1} lowering of the bands 1625 cm^{-1} with shoulder at 1615 cm^{-1} assigned to symmetric and antisymmetric modes of azomethine linkage show the coordination[24] of nitrogen of azomethine group.

The ionic halides do not exert any detectable effect in the IR spectra in the conventional region. The appearance of sharp band at ~ 1770 cm^{-1} assignable to ionic nitrato group and band at ~ 2110 and 2370 cm indicate the ionic thiocyanato group[25]. Which confirms the presence of anions outside the coordination sphere.

Thus it is obvious from the IR spectra that coordination may occur through two pyridine nitrogen and four azomethine nitrogen atoms.

Magnetic and Electronic Spectral Studies

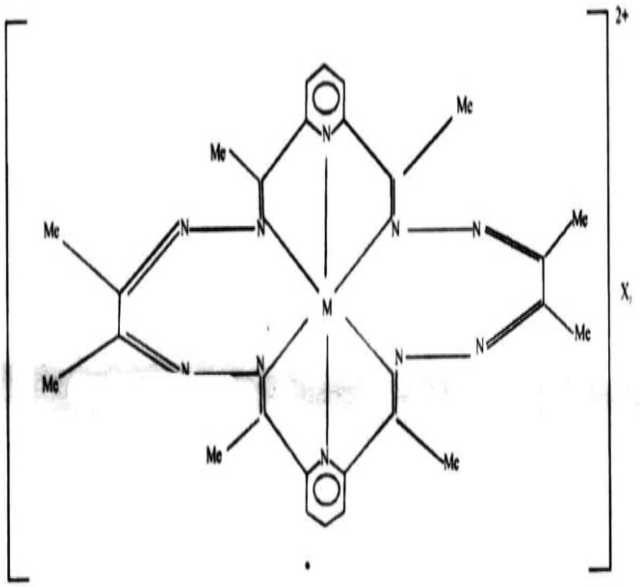
The values of magnetic moment of Fe (II) complexes lie in the range 5.42-5.85 BM at room temperature (300K), and are well consistent to the six coordinated octahedral complexes 26.

The electronic spectra of these complexes show bands in the region ~ 8510-8900 cm^{-1} and 1150-12550 cm^{-1}. The bands are splitting of a single band and may be assigned $^5T_{2g}$?^5E_g. The splitting of ^5E_g state may be due to distortion of

octahedron but steric distortion of octahedron is not expected in molecule having T_{2g} ground state[27]. In these complexes the splitting of the spin allowed band attributable only to Jahn - Teller effect and all other explanations seem to be invalid. If approximations are made the spectra is consistent to a distorted octahedral geometry[28] around the Fe (II) metal.

The magnetic moment of Co (II) chelates observed in the range 4.48-4.65 BM at room temperature and is consistent to the octahedral geometry around the Co (II) metal[26]. The solution spectra of Co (II) chelates exhibit absorption in the region ~8100-9100 cm^{-1}(v_1), 15250-15750 cm^{-1}(v_2) and 18700-20250cm^{-1} (v_3). The spectra show octahedral geometry as reported earlier[20]. Thus assuming the effective geometry to be D_{4h}, the bands can be assigned to $^4T_{1g}$?$^4T_{2g}$ (F), $^4T_{1g}$-$^4T_{2g}$(F) and$^4T_{1g}$?$^4T_{1g}$(P) for v_1,v_2,v_3 respectively. The values of various field parameters Dq, B, ? calculated (Table-2). The spectrochemical series can be drawn as NCS NO, halids.

The magnetic susceptibility at room temperature of Ni(II) chelates lie in the range 2.96-3.10 BM. The values are well within the range postulated for six coordinate octahedral chelates[29]. The solution spectra of Ni (II) chelates show discenerable bands with shoulder on low energy side. Other two bands appear in the region -16700-17100 cm^{-1} (v_2) and 27800-28250 cm^{-1} (v_3), are assigned to $^3A_{2g}$?$^3T_{1g}$ (F) and $^3A_{2g}$?$^3T_{1g}$ (F) v_2 and V_3, respectively. The first two bands are split in one band and v_1 are in the region-9700-10300 cm^{-1} and 11750- 12300 cm^{-1}, can be assigned to $^3B_{1g}$?^3E_g and $^3B_{1g}$?$^3B_{2g}$ transistions[30]. The other two bands are not affected by low symmetry field. The reason for v2 and v_1 is that the related terms are $^3T_{1g}$ (F) and $^3T_{1g}$(P), both give ($^3A_{2g}$+ ^3E_g) in D_{4h} Symmetry and the two level split in the reverse sense in the strong field limit. The interpretation is well accordance to the octahedral geometry[31]. The calculated values of various parameters are given in Table-3. Based on analysis, conductance measurements, magnetic electronic and IR Spectral studies, following structure may be proposed for these complexes.



M=Fe(II), Co(II) or Ni (II) ; X = Cl, Br, NO_3 or NCS,

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TABLE 1: Analytical data of divalent iron, cobalt and nickel chelates

Chelates	Colour	M	C	H	N	X	ÄMhos Cm $^{-2}$ mol^{-1}	Nol.Wt.
1	2	3	4	5	6	7	8	9
[Fe(C H N)]Cl	Brown-red	9.81 (919)	51.56 (51.23)	4.52 (4.92)	22.66 (22.98)	11.76 (11.65)	141	(609)
[Fe(C H N)]Br	Orange-red	8.23 (8.02)	44.77 (44.69)	4.53 (4.29)	20.56 (20.05)	22.84 (22.92)	154	(698)
[Fe(C H N)](NO)	Brown	8.52 (8.45)	47.61 (47.12)	4.49 (4.53)	——— (25.37)	18.81 (18.73)	164	(662)
[Fe(C H N)](NCS)	Brown-red	8.15 (8.56)	51.41 (51.37)	4.33 (4.58)	25.89 (25.68)	——— (17.73)	161	(654)
[Co(C H N)]Cl	Red-pink	9.18 (9.64)	50.67 (50.98)	4.53 (4.90)	22.64 (22.87)	11.87 (11.60)	151	(612)
[Co(C H N)]Br	Brown-yellow	8.00 (8.41)	44.99 (44.50)	4.74 (4.27)	——- (19.97)	22.66 (22.82)	159	(701)
[Co(C H N)](NO)	Brown	8.63 (8.87)	46.61 (46.91)	4.81 (4.51)	25.52 (25.26)	18.82 (18.64)	155	(665)
[Co(C H N)](NCS)	Brown-red	8.80 (8.98)	51.00 (51.14)	4.62 (4.56)	25.92 (25.57)	——— (17.65)	162	(657)
[Ni(C H N)]Cl	Dark green	9.53 (9.64)	———- (50.98)	———- (4.90)	22.26 (22.87)	11.42 (11.60)	1441	(612)
[Ni(C H N)]Br	Green	8.69 (8.41)	44.41 (44.50)	4.58 (4.27)	19.87 (19.97)	22.79 (22.82)	148	(701)
[Ni(C H N)](NO)	Black-green	8.15 (8.87)	46.19 (46.91)	4.59 (4.51)	——— (25.26)	18.04 (18.64)	151	(665)
[Ni(C H N)](NCS)	Dark green	8.51 (9.98)	51.55 (51.14)	4.13 (4.56)	25.47 (25.57)	——— (17.65)	149	(657)

TABLE 2: Magnetic and electronic spectral data of divalent cobalt chelates

Chelates	Spectral Bands (cm^{-1})	Dq	B	C	β	V_1/v_2	Calcd. bands (cm^{-1})		μeff.BM(300K)
[Co(C H N)]Cl	85550,15250,18700	1069	819	-	8.84	1.78	-	-	4.65
[Co(C H N)]Br	9100,15750,19650	1137	855	-	0.88	1.73	-	-	4.57
[Co(C H N)](NO)	8100,15250,19050	1012	865	-	0.89	1.88	-	-	4.52
[Co(C H N)](NCS)	8700,15700,20250	1087	915	-	0.94	1.88	-	-	4.48

TABLE 3: Magnetic and electronic spectral data of divalent nickel chelates

Chelates	Spectral Bands (cm^{-1})	Dq	Dt	DT	DQ	DT/DQ	μeff.BM(300K)
[Ni(C H N)]Cl	9900,11750,71750,28150	1175	211	2859	28928	0.09	2.98
[Ni(C H N)]Br	100500,12000,16700,28250	1200	222	3008	29439	0.10	3.10
[Ni(C H N)](NO)	10300,12300,17000,27800	1230	228	3089	30168	0.10	3.08
[Ni(C H N)](NCS)	9700,12200,16850,28000	1220	285	3862	28979	0.13	2.96

REFERENCES

1. Curtis, NF.,Coord. Chem. Rev., 3,3 (1968)
2. Lindoy, L.F., Bush, D.H, in W.L. Jolly (Ed.) PreperativeInorgReac, 6(1971),
3. Kumar, Ajay, PhD Thesis, Meerut Univ Meerut (1991)
4. Drew, M.G.B., Nelson, J., Esho, F., Mackee, V., Nelson, SN, J.Chem. Soc. (Dalton), 1837 (1982).
5. Jager, E.Z., Chem., 8, 392 (1968), Z. AnorgAlleChem, 364, 177 (1969)
6. Goedken, V.L., Case, J.M., Whang, YA. J. Chem. Soc., Comm, 377 (1973)
7. Howaldar, M.B.H., Islam, M.S., Karim, M.R., Ind. J. Chem., 39A, 407 (2000)
8. Rana, V.B., and Teotia, MP, Ind. J. Chem. 19A, 267 (1980)
9. Chandra, S. Gupta, K., Ind., J. Chem. 40A, 775 (2001)
10. Rana, V.B., (Mrs) Singh P., Singh, D.P. and Teotia, M.P., Polyhedron, 1, 377 (1982)

11. Rana, V.B. (Mrs) Singh, P., Singh, D.P. and Teotia, M.P., Trans. Met. Chem., 7, 174 (1982).
12. Kumar, Ajay, Kumar, Gajendera, Kumar, Amit, Shishodia, Nupur and Rana, V.B., Ind. J. Chem
13. Basch, D.H., Bailar, J.C. (le), JAm. Chem. Soc., 78, 1137 (1956).
14. Mac Collum, D.C., Hall, L. White, C., Ostrandes, R., Rheingold, A., Whelan, J. and Bosnick, B. Inorg. Chem., 33, 924 (1924).
15. Chandra, S., Singh, R., Ind. J. Chem., 34A, 1003 (1995).
16. House, DA, Curtis, N.F., J. Am. Chem. Soc., 86, 1331 (1964).
17. Nakamoto, K., "Infrared Spectra of Inorganic and Coordination compounds", 2" Ed. (Wiley Inter Science Newyork) (1970).
18. Rana V.B., Singh, D.P., (Mrs) Singh P. and Teotia, M.P., Trans Met. Chem. 6,36 (1981).
19. Singh, N.IK, Kushwaha, S.K., Trans. Met. Chem., 26, 140 (2001)
20. Singh, B., Singh, R., Chaudhary, R. V. and Thakur, K.P., Ind. J. Chem., 11, 174 (1973).
21. Gill, N.S., Kingdon, HJ, Aust. J. Chem., 19, 2197 (1966).
22. Curtis, N.F., Flood, K. Ward, R.T., Polyhedron, 25, 1313 (2006)
23. Dus, S.K., Rastogi, D.K. and Sahni, S.K., J. Inorg. Nucl. Chem., 42, 1711 (1980).
24. Chandra, Sulekh, Jain, Deepali, Sarkar, Anjana and Anupama, J. Ind. Chem Soc. 86, 220 (2009)
25. Adom, D.M., 'Metal Ligand and Related Vibrations' (E. Arnold, London) (1967)
26. Figgis, B.N. and Lewis, J., Prog, Inorg. Chem., 6, 37 (1965).
27. Lever, A.B.P., Inorganic Electronic Spectroscopy, Elsevier, Amstredam (1968).
28. Carvahlo, S, Delgado, R., Draw, DG.M., Vitor, F., Fuguria, M. and Henrigues, RJ, Polylderon, XXX (2007)
29. Flipen, R.B., Friedberg, S.A., Phy Rev., 121, 1541 (1961).
30. Lever, A.B.P, ACS Advances in Chem, No. 62, 430 (1967),
31. Lever, A.B.P., Nelson, S.M. and Shepared, T.M., Inorg. Chem., 4, 816 (1965).

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