

# Study of Waste Water Effluent Characteristics Generated from Paper Industries

Shivnarayan Singh

*M.tech Environmental Engineering and Management, IV Sem. Student, Subharti Institute of Technology and Engineering Swami Vivekanda Subharti University, Meerut-250005 (Uttar Pradesh)*  
*E-mail: s.rana344@gmail.com*

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**Abstract**—This paper show the physico-chemical characteristics of effluent discharge from paper and pulp industry. The effluent from the paper industry is characterized by high amount of COD, BOD, TDS, pH, SS, Colour. The samples were collected from the inlet and outlet of the effluent treatment plant of paper mill. The samples were analyzed and compared with the Indian standards of effluent discharge. The effluent before treatment average range contains pH of  $8.5 \pm 0.278$ , Suspended Solids of  $1720.33 \pm 253$  mg/l, Total Dissolved Solids average ranges from  $2658.33 \pm 81.44$  mg/l, Colour value is  $735 \pm 108.28$  PCU, COD and BOD varies  $2420 \pm 259.55$  mg/l and  $778.33 \pm 43.10$  mg/l simultaneously. After the treatment of waste water average value of pH is  $7.65 \pm 0.13$ , Suspended Solids  $58.33 \pm 7.63$  mg/l, Total dissolved solids ranges from  $1918.33 \pm 67.88$  mg/l, Colour value is  $224.16 \pm 3.60$  PCU, COD and BOD ranges from  $214 \pm 1.73$  mg/l and  $24 \pm 1$  mg/l, respectively. Result shows that the pH, SS, TDS, Colour, COD, BOD, within the permissible standards after treatment. The paper mill meets all these Norms as per set by Central Pollution Control Board, India.

**Keywords:** pH, TDS, TSS, COD, BOD, Paper industry.

## 1. INTRODUCTION

Water (H<sub>2</sub>O) is formed by the catalytic introduction of 2 molecules of hydrogen and one molecule of oxygen and earth and not other planetary bodies has any trace of water while theories on origin of water may continue, its essentiality for all life forms as known on earth cannot be Questioned. Out of 122 countries, India ranks 120th in terms of water quality. At least 200 million Indian citizens do not have access to safe clean water. It is estimated that 90% water resources in the country are contaminated with untreated industries, domestic water pesticides and fertilizers. India therefore faces a substantial challenge to meet the legal and moral obligations towards the provision of safe water. The paper industry is the largest industry in India [1]. Among world it ranks 20th paper producing country. [2]. These industries disturbing the ecological balance of the environment by discharging a wide variety of wastewater. Depending upon the nature of raw material, the wastewater is generated per metric tonne of paper produced [3]. "Wastewater," also known as "sewage," originates from household wastes, human and animal wastes, industrial wastewaters, storm runoff, and

groundwater infiltration. Wastewater, basically, is the flow of used water from a community. The nature of wastewater includes physical, chemical, and biological characteristics which depend on the water usage in the community, the industrial and commercial contributions, weather, and infiltration/inflow. It is 99.94 percent water by weight (Water Pollution Control Federation 1980) [4]. The remaining 0.06 percent is material dissolved or suspended in the water. The dissolved and suspended solids in wastewater contain organic and inorganic material. Organic matter may include carbohydrates, fats, oils, grease, surfactants, proteins, pesticides and agricultural chemicals, volatile organic compounds, and other toxic chemicals. Inorganic matter may cover heavy metals, nutrients (nitrogen and phosphorus), pH, alkalinity, chlorides, sulphur, and other inorganic pollutants. Gases such as carbon dioxide, nitrogen, oxygen, hydrogen sulphide, and methane may be present in wastewater (Lee and Lin, 2000) [5]. Wastewaters is normally treated by a combination of physical-chemical and biological operations. However, it is possible to treat waste waters solely with physical-chemical methods (Droste, 2004) [6]. Industries is the major sources of pollution in all environments. Based on the type of industry, various levels of pollutants can be discharged into the environment directly or indirectly through public sewer lines. Wastewater from industries includes employees' process wastes, sanitary wastage, generate from manufacturing units, washing waters and relatively uncontaminated water from boilers and cooling tower operations. A rapid industrialization has lead to the industrial effluents and sewage, resulting in water pollution which leads to water crisis in India and all over the world. The effluent stream coming out of the industries is mainly comprised of hazardous chemicals and heavy metal ions such as chromium, nickel, copper, lead, arsenic, etc. Heavy metals are very toxic in nature and harmful to the environment. The pulp and paper industry uses large quantity of freshwater and lingo-cellulosic materials in the process of production of paper and it generates large amount of influent. The generated effluent is characterized by dark color, foul odour, high organic content and extreme quantities of chemical oxygen demand

(COD), biochemical oxygen demand (BOD) and pH. The dark color in paper mill effluent is caused by the organic ligands such as wood extractives, resins, synthetic dyes, tannins, lignin and its degradation products. The dark color in untreated effluent is a major environmental concern as its discharge to water bodies inhibits the photosynthetic activity of aquatic biota by reducing sunlight, besides exhibiting the toxic effects on biota.

## 2. METHODOLOGY

### 2.1. Collection of samples

The samples for the analysis was collected from the effluent treatment plant of agro based paper industry of Muzaffarnagar. The wastewater samples were collected from the inlet (raw wastewater) and outlet (final treated wastewater) of the effluent treatment plant of the paper mill for analysis. Sampling was done over a period of twice in a month. The samples were collected during February 2015 to April 2015 in fifteen days interval, respectively. The grab samples were collected in the plastic containers which were refrigerated at 4° C prior to further treatment. The samples were analyzed using standard methods of analysis of water and wastewater of APHA [7]. Effluents samples collected from craft paper mill were analyzed for the required parameters in order to evaluate the pollution load of water streams in which they are thrown. The physicochemical analysis in laboratory for the following parameters and analysed using standard methods given in table 1:

**Table 1: Analytical methods for physico-chemical parameters of pulp and paper mill effluents**

S. NO.	PHYSICO-CHEMICAL PARAMETERS	METHOD APPLIED FOR LABORATORY ANALYSIS
1.	pH	Handy pH meter
2.	Total suspended solids (TSS)	Gravimetric, residue drying 100° C
3.	Total dissolve solids (TDS)	Gravimetric, oven drying at 100° C
4.	Chemical oxygen demand (COD)	Potassium dichromate , closed reflux method
5.	(Biochemical oxygen demand) (BOD)	5 days incubation at 200C
6.	COLOUR	Spectrophotometer

## 3. RESULTS

Paper industries are based on craft based raw material used to manufacturing paper production and as their discharge norms are as per charter by central pollution control board. Understanding the nature of wastewater is fundamental to design appropriate wastewater treatment process, to adopt an appropriate procedure, determination of acceptable criteria for the residues, determination of a degree of evaluation required to validate the procedure and decision on the residues to be

tested based on toxicity. So it is necessary to ensure the safety, efficacy, quality of the treated wastewater. Finally after treatment of waste water it is being used in for gardening and plantation, and some recycled water used in the plant for pulping process of pulper, high pressure spray shower, vacuums etc and it is necessary to utilized treated water to save earth water for our future generation.

### 3.1 pH

The hydrogen-ion concentration is an important parameter to check the quality of effluent discharge from the plant or to a measure of acidity and alkaline of an aqueous solution. The pH of the influent (raw effluent) was measured to be 8.6-9.15 which is alkaline as reported<sup>7</sup> compared to 7.5-7.8 with treated effluent. Low value of pH is due to the metabolism of fungus, micro flora and activities of microbial population [8].

### 3.2 Suspended Solids

The concentration of suspended solids measured from inlet of ETP ranges from 1470-1976 mg/l after treatment the concentration of suspended solids measured from effluent ranges from 50-65 mg/l respectively.

### 3.3 Total Dissolved Solids

The total dissolved solids concentration varied from inlet 2565-2715 mg/l whereas from treated effluent varied from 1840-1960 mg/l respectively. The values shows TDS are in permissible limit as compared with Pollution Board standards

### 3.4 COD and BOD

Chemical Oxygen Demand is the measure of amount of oxygen required to breakdown both organic and inorganic matters and biological Oxygen Demand is the measure of the oxygen required by microorganisms whilst breaking down organic matter. BOD measures the organic loading of streams and thereby quantifies the dissolved oxygen levels. The COD and BOD levels of influent effluent varied from 2125-2615 mg/l and 740-825 mg/l respectively. Whereas the COD and BOD levels of effluent varied from 212-215 mg/l and 23-25 mg/l respectively. The levels of COD and BOD is reduced to certain extent by biological treatment process for which the effluent is treated which consists of equalization, primary clarifier , aeration tank and the secondary clarifier. Biological treatment process results in oxidation of organic matter, which provides energy for microbial metabolic process<sup>6</sup>. The value of discharge effluent within the permissible limit set by Central Pollution Control Board, India to discharge for irrigation.

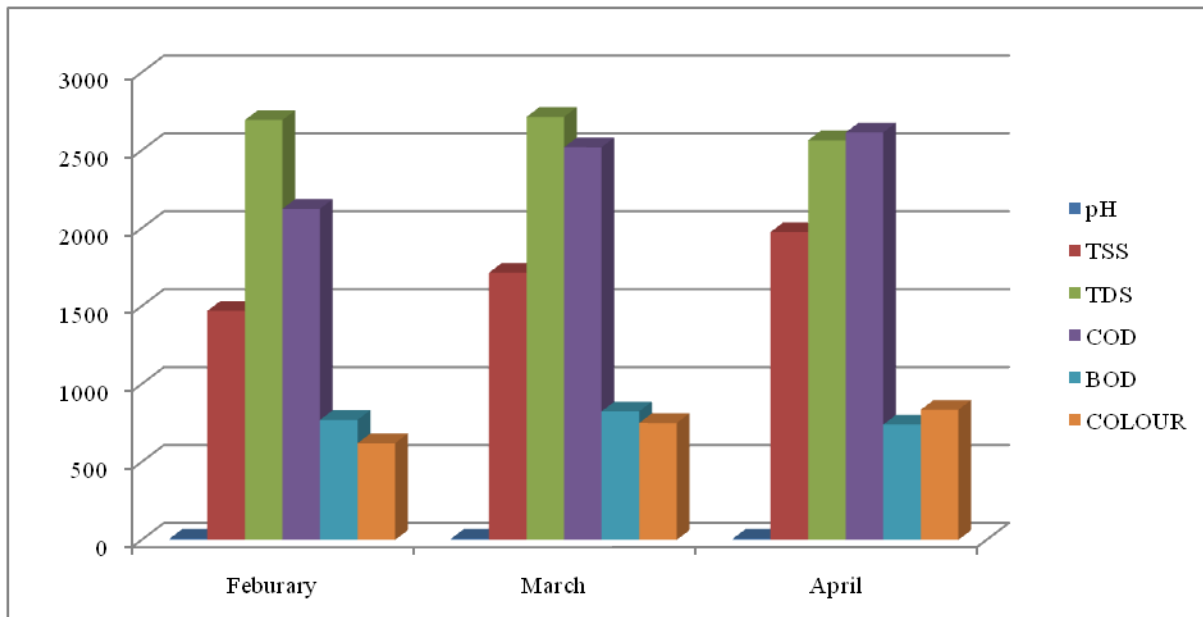
### 3.5 Colour

The colour is usually the first contaminant to be recognized in effluents that affects the aesthetics, water transparency and gas solubility of water bodies [9]. This colour is due the high concentration of lignin content in the outlet sample. Colour derived from lignin is an indicator of the presence of

potentially inhibitory compounds and in addition, may have direct inhibitory effects on some of the lower organisms in the food chain. The colour of the effluent typically depends upon the different industrial processes. The final outlet of the water treatment plant has the value of 220-227.5 pt.co units.

**Table 2: Average of variations of different physiochemical parameters in influent from Inlet of paper mill**

PARAMETERS	FEBRUARY	MARCH	APRIL	MEAN WITH S.D
pH	8.8	9.15	8.6	8.85 ± 0.278
TSS	1470	1715	1976	1720.33 ± 253
TDS	2695	2715	2565	2658.33 ± 81.44
COD	2125	2520	2615	2420 ± 259.55
BOD	770	825	740	778.33 ± 43.10
COLOR	620	750	835	735 ± 108.28



**Fig. 1: Bar graph of Average of variations of different physiochemical parameters in effluent from Inlet of paper mill**

**Table 3: Average of variations of different physiochemical parameters in effluent from Outlet of paper mill:**

PARAMETERS	FEBRUARY	MARCH	APRIL	MEAN WITH S.D
pH	7.55	7.6	7.8	7.65 ± 0.13
TSS	65	60	50	58.33 ± 7.63
TDS	1960	1955	1840	1918.33 ± 67.88
COD	215	212	215	214 ± 1.73
BOD	24	25	23	24 ± 1
COLOR	227.5	225	220	224.16 ± 3.60

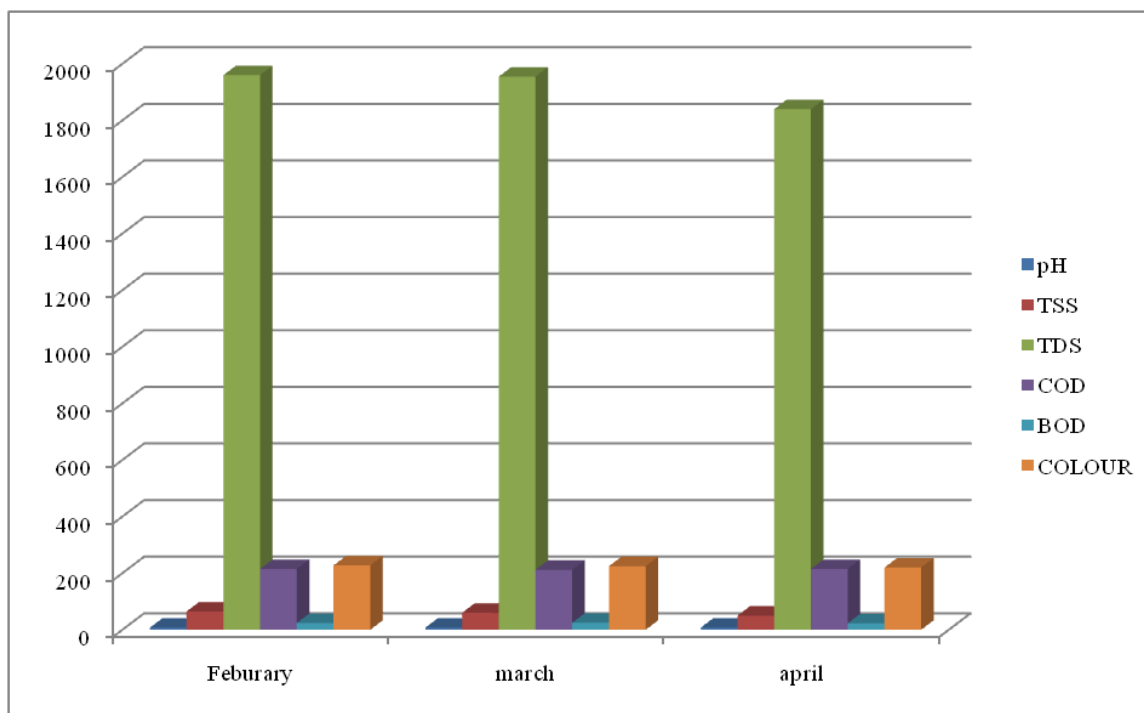


Fig. 2: Bar graph of Average of variations of different physiochemical parameters in effluent from Inlet of paper mill

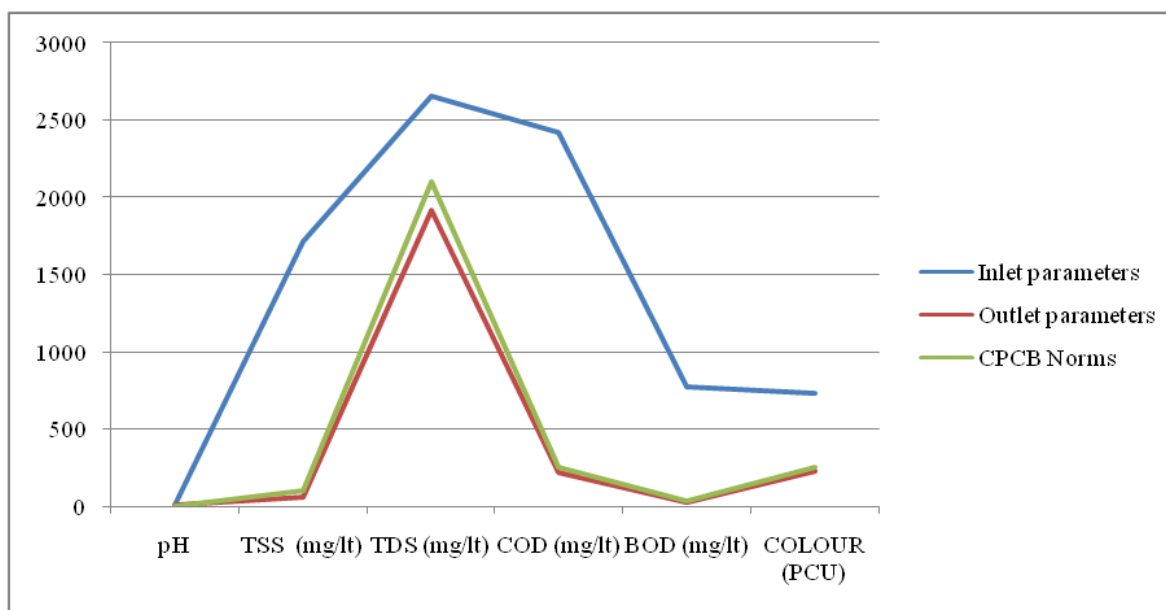


Fig. 3: Comparatives Line graph of inlet parameters, outlet parameter of paper industry with CPCB Norms.

On the basis of above discussion it is concluded that the effluent discharged from paper industry in the selected area was within the permissible ranges of the standards of CPCB, but proper strategies can be used to treat the effluent prior to its disposal to the environment.

The paper mill is growing fast and produces different varieties of paper. The physico-chemical characteristics of effluent from this mill revealed that the effluent is light brown in colour, pH shows alkaline nature of the effluent, SS, BOD, COD are the parameters from the treated effluent is under norms in concentrations compared to CPCB (Central pollution Board) standards.

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# Remediation Techniques, for Open Dump Sites, used for the Disposal of Municipal Solid Waste in India

Mayurika Chakrabarti<sup>1</sup> and Amit Dubey<sup>2</sup>

<sup>1</sup>CEPT University

<sup>2</sup>SPIPA, Ahmedabad

E-mail: <sup>1</sup>mayurika92@gmail.com, <sup>2</sup>dubey.amit12@hotmail.com

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**Abstract**—Open Dumping of Municipal Solid waste which is the widely practiced method for disposal of the same has time and again proven to pose threats on multiple fronts, such as environmental pollution encompassing soil contamination, air pollution, water pollution; an ever so potent source of disease outbreak and finally, degrading the overall surrounding in the nearby vicinity. Many incidences of the negative impact of open dumping have come to the light in terms of water contamination, heavy degradation of air quality, surrounding soil contamination leading to negative impacts on its value for agriculture and commerce. These challenges have time and again, called for methods to neutralize them and prevent damages to the maximum possible extent. These methods, typically referred to as 'remediation', meaning 'to correct', have been thought over since decades and many different approaches have evolved during the process. The following is a documentation of the better established remediation techniques, which are suitable for dump sites containing one or the other kind of refuse, depending on the characteristics of the waste. The suitability of the discussed techniques has further been contemplated with relation to the Indian context where-in, like most developing countries, waste segregation is to a very low extent.

## 1. INTRODUCTION

Various methods of remediation can be deployed to neutralize the ill effects of the dump sites, and the threat they pose to the environment at large. Dump site remediation, in essence, is the operation of nullifying the ill impacts of the dump on the environment and simultaneously recovering utilizable material as and when possible. Some of the methods deployed to remediate MSW dumps are temporary solutions while others are of a more permanent nature unless subjected to large forces.

Some of the mainstream remediation processes are landfill capping and closure, in-situ vitrification, sub-surface cut-off walls, and Landfill mining.

## 2. SCOPE, OBJECTIVE AND METHODOLOGY

### 2.1 Objective

The objective of the paper is to study and assess the suitability of remediation techniques for open dumpsites used for the

disposal of Municipal Solid Waste in state capitals and metro cities around India.

### 2.2 Scope of Work

Scope of the work includes studying the types of remediation techniques for open dumpsites used for the disposal of Municipal Solid Waste and assessing their suitability.

### 2.3 Methodology

The objective of the paper being the study of the remediation techniques for open dumpsites used for the disposal of MSW in India, the approach taken up was to find out about the various methods deployed at other open dumpsites and the probable suitable methods with respect to the Indian scenario.

## 3. REMEDIATION TECHNIQUES

### 3.1 Landfill Capping and Closure

Capping and closure of landfill essentially includes creating a bifurcating layer between the accumulated waste and the environment, humans and other animals, protecting them from the adverse effects of the contaminated waste that is accumulated and is also believed to limit the migration of the harmful contents.

As per guidelines, caps are of two types, of which those used for landfills containing hazardous materials include three layers, wherein the top layer is soil that can support native vegetation, the middle layer is a drainage layer and the bottom most and third layer consists of an impervious synthetic covering over a compacted two feel thick layer of clay. The design of the cap is strongly influenced by the gas release mechanism that is to be adopted for the letting out of the gases produced as a result of the decomposition of the waste inside.

A major concern with the capping method is that its life is 50-100 years which is relatively less when the neutralization of

the underlying waste might take much more time than that, and make the underlying matter non-hazardous.

### 3.2 In-situ Vitrification

This technology is deployed when the wastes deposited in the dump are of such nature that their degradation period is too long and they pose dire threats to the environment and other living beings. This technology ensures the entrapping of the wastes into a completely impervious monolithic enclosure and render them completely in-effective what so ever.

The process typically involves graphite electrodes hammered into the dump, at the corners of a square layout on plan. A very high capacity generator or a direct line from the grid is connected to the electrode and the arc (electricity) is allowed to jump from one electrode to other. When the arc passes through the soils and wastes it produces tremendous heat and reduces the soil into molten mass. As the mass below and around the electrodes turns liquid, the electrodes sink deeper and in-turn more of the matter is liquefied. When the entire of the electrodes have sunk within the molten mass, and is not possible for them to penetrate deeper, the electricity is shut off and the molten mass is allowed to cool down, turning into a glass cube entrapping all the waste in between along with the electrodes. The depth of vitrification is governed by the amount of electric power that is available and the depth of the graphite electrodes.

Various materials of those disposed off in the dump react in different manner to the vitrification process. Organics are generally converted into gasses and these gasses rise to the top, and are collected in gas collectors placed at the top. This gas is treated at gas treatment centre to neutralize the volatile substances in them. The rest of the matter gets entombed within the glass. Nuclear wastes can also be neutralized by this method as the glass thickness also aids in obstructing the radiation upto significant levels. The formation of glass also removes almost all of the voids within the waste mass, and leads to almost 20-50% of volume reduction (Study on the Various Methods of Landfill Remediation, Vasudevan, Naveen. K, et al, 2003).

Compared to the conventional processes vitrification is much quicker, and a one-step process.

### 3.3 Sub Surface cut-off walls

These systems are akin to cut-off walls used for the containment of water in some enclosed volume. The cut-off walls for MSW dump sites are usually designed to separate the waste dump from any underlying water stream/source. It is usually done by grouting with any impervious material such as cement, concrete, bentonite, bentonite slurry, bentonite cement slurries, geo-membranes etc. (Study on the Various Methods of Landfill Remediation, Vasudevan, Naveen. K, et al, 2003).

### 3.4 Landfill Mining

Landfill mining is the process of excavating from an operating or closed solid waste landfills, and sorting the unearthed materials for recycling, processing, or for other dispositions (Lee and Jones, 1990; Cosu et al 1996; Hogland et al, 1998; Carius et al, 1996). It is the process whereby solid waste that has been previously land filled is excavated and processed (Strange, 1998).

Landfill mining essentially deploys the same methods as open mining to reclaim the refuse that has been accumulated in a waste dump or landfill. This excavated refuse is then sorted through a screening machine to separate the larger pieces from the smaller ones. Large pieces of refuse generally consist of tyres, and stones and the small ones are generally paper and plastics.

The objectives with which Landfill mining is resorted to can be listed as follows:

- i. Conservation of landfill space
- ii. Reduction in Landfill area
- iii. Elimination of potential contamination source
- iv. Rehabilitation of dump sites
- v. Energy recovery from recovered wastes
- vi. Reuse of recovered materials
- vii. Reduction in waste management costs
- viii. Redevelopment of landfill sites

(Hogland et al, 1997)

Landfill mining also remediates the dump by removing the entire accumulated waste thereby enhancing the overall hygiene and quality of that patch of land and the surroundings. As a second option, it also facilitates the placing of an impervious liner and replacing the collected waste, thus preventing any leachate from polluting the soil or the ground water, and makes it manageable to introduce proper waste management measures.

Landfill mining deploys mechanical segregation to reclaim one or more of the below stated materials:

- i. Landfill Volume
- ii. Soil enricher/Compost
- iii. Wood
- iv. Recyclable metals such as iron, aluminium, etc.
- v. Concrete, and bricks for use in roads etc.

Traditionally, a setup involving a conveyor and a trommel for segregating the excavated material into oversized, under sized and intermediate portion is the key step in any landfill mining operation. The undersized fine fraction generally consists of soil and humus, oversized matter is composed of metals, textiles, rubber and plastics, intermediate sized fraction is made up of combustible materials, recyclable materials and decomposed organic matter upto some extent. Ferrous metals

are generally taken off the stream by deploying a magnetic separator and an air classifier arrangement is put in place to separate the non-ferrous metallic portion, leaving behind combustible fraction from the waste.

A landfill mining project usually consists of an excavator that removes the deposited matter from the dump. The bulky pieces are then removed from the excavated stuff and smaller stockpiles which are easier to handle are made using a front end loader. A trommel is then deployed to physically segregate the soil and solid waste. Trommel screens are much more effective than vibrating screens for basic project (Murphy 1993). The size and type of the screen deployed depend on the end use of the recovered material. A 6.25 mm screen for example, would be deployed when the reclaimed soil is to be used for landfill cover, where as a 2.5mm sieve would be deployed when tiny fractions of metals, plastics, glass etc. are to be recovered from within a large soil fraction. The efficiency of the material recovery is largely governed by the waste composition, mining technology and the efficiency of the segregation technology.

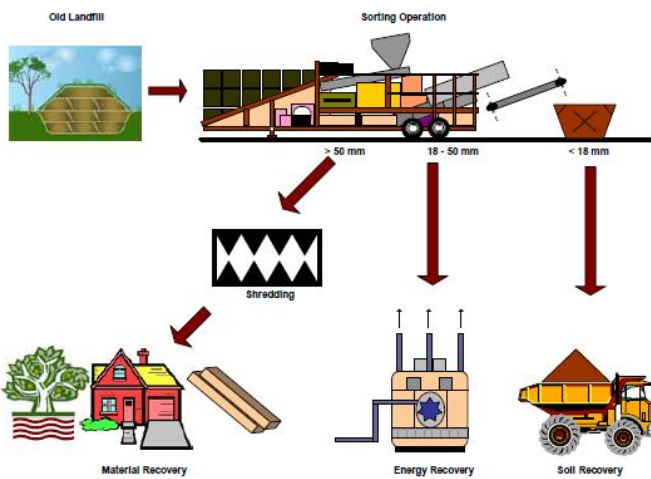


Fig. 1 Schematic of landfill mining process (Carius et al, 1999)

The recovery of various materials ranges from 50 to 90% of the waste (Strange, 1998). The average of soil fraction in MSW landfills is observed to be around 50-60%, however it can vary between 20 and 80% depending on moisture content and decomposition rate (Hogland, 2002). The soil fraction can be used as cover or lining of new landfill. Landfill needs to be 15 years old before a successful mining project can be performed (Strange, 1998).

**3.4.1 Benefits of Landfill Mining**

Landfill mining carried out with the objective of reclamation extends the life of the landfill by decreasing the volume through the removal of recoverable material, combustion of suitable material and compaction. Potential benefits include the following:

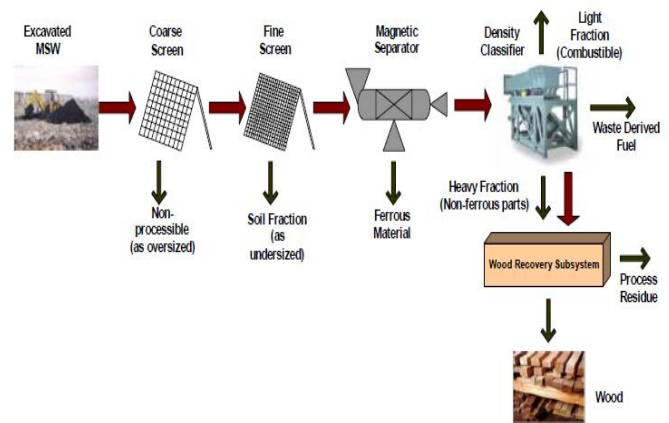


Fig. 2: Process Scheme for a landfill mining plant (Savage and Diaz,1994)

- i. Recovered materials such as ferrous metals, plastic, aluminium, and glass can be sold if markets exist for these materials.
- ii. Reclaimed soil can be used on site as daily cover material on other landfill cells, thus avoiding the cost of importing cover material. Also a market might exist for reclaimed soil for use in other applications such as compost.
- iii. Combustible reclaimed waste can be mixed with fresh waste and burned to produce energy.
- iv. By reducing the size of the landfill footprint through cell reclamation the facility operator may also be able to either lower the cost of closing the landfill or make land available for other uses.
- v. Hazardous wastes if uncovered during LFMR, especially at older landfills, could be managed in an environmentally sound manner.

(Hogland et al, 1997)

The most relevant benefits of any landfill mining operation in economic terms are more often than not, indirect, and can be summarised as follows:

- i. Reclaimed volume for disposal of solid waste
- ii. Decreased or completely avoided expense of any closure procedure and the monitoring that follows such closure procedures.
- iii. Revenues can be generated by the sale of the reclaimed materials such as recyclable metals, plastics etc. Combustible material can be processed into fuel and the soil fraction can be used as compost, or for filling in construction projects or as cover soil for new cells, thus avoiding the cost of virgin soil and protecting a natural resource (fertile soil)



- iv. The value of the land that is thus reclaimed, when deployed for other uses.

The most direct and impactful of these benefits for large municipalities facing land scarcity is the freeing up of the landfill capacity avoiding on all the time and money that would be invested to come up with a new site for disposing of the solid wastes. Though, for Indian context, the benefits are multi-fold in the sense that majority of the solid waste disposal in India is done in open dumpsites, which constantly contribute to degrading the environment on some scale, which can be remediated by deploying a landfill mining project, and preventing any further contamination from happening, thus conserving our already scarce natural resources such as water and land.

### 3.4.2 History of Landfill Mining

Since the first instance of Landfill mining, carried out in 1953 in Tel Aviv, Israel, it has widely been deployed as the preferred mode of sustainable landfill management. The operation deployed in Tel Aviv was taken up with the sole objective of reclaiming soil fraction which was to be utilized as soil improvement for citrus orchards. The equipments deployed were a front end loader, clamshell, conveyors and a rotating trommel screen. The trommel had openings of 25mm and a length of 7m with a 2m diameter and was rotated at the speed of 13rpm. The fraction that was retained on the screen was sent away for manual sorting to recover ferrous materials, and other matter for recycling.

Though the first landfill mining operation was carried out way back in 1953, the first well documented operation was undertaken in 1988, Collier County in Florida. The major objective of this operation was to eliminate a potential pollution source that could degrade the quality of ground water, recovering soil for use as cover material for the active cells, and to recover landfill volume. Receiving around 4,00,000 tons of refuse every year, the landfill was estimated to have a capacity to cater for another 9 years. After the mining operation it was found that the dirt and humus portion was almost 60-70% of the total excavated refuse. 15% of the dug up refuse was intermediate sized fraction composed of majorly plastic, textile, wood, glass, aluminium, rubber and brass and was found to have a significant calorific value. The intermediate sized fraction thus presented opportunity for further recycling and processing and selling those materials in the market generating revenue.

By mining the unlined portion of the landfill which was 20 years old, reclaiming and removing the refuse from there and selling the saleable fraction or utilizing the soil, the Collier County managed to lower their landfill operating costs significantly and extend the life of the landfill. Though, the most important outcome of the entire operation was the remediation of a potential pollution source that was posing threat to the ground water.

Since 1988, i.e. after the Collier County operation, landfill mining gained a new momentum globally, and has been experimented with numerous times.

### 3.4.3 Case studies from Asia

#### 3.4.3.1. Landfill Mining in China

In china, experiments have been carried out where-in landfill mining and horticulture has been combined. Trials were performed at Sai Lin, after an extremely fertile soil fraction and incombustible inorganic fraction was encountered on visual inspection. Following this, old cells of the landfill were excavated, and the biodegraded soil fraction, combustible inorganic fraction and remaining incombustible fraction were separated by screening. The cells thus emptied were lined with impervious layer, and new gas and leachate collection systems were installed. The residual incombustible portion of the excavated waste was deposited back into the upgraded cells. The recovered soil was mixed with excavated virgin silt and the bund wall trimmings, and yielded an extremely fertile mixture used for the final cover and the basis for the horticulture program (Dumpsite Rehabilitation and Landfill Mining, Asian Regional Research Program on Environment Technology (ARRPET), Kurien, J. et al, 2004). The upgraded cells were then used as biological reactors and the degradation process within was accelerated by leachate recycling and drainage and resulted into larger methane yield. The cells that were completed were topped with greenhouses constructed on them, and horticulture activities were carried out there. The methane gather from the cells was used to fuel a waste to energy plant along with other combustible fraction recovered from the mining operation and produced electricity for local consumption or sale to the electricity grid. Excess heat was used for keeping the temperatures of the greenhouses elevated all through the year for better production of the horticulture products.

#### 3.4.3.2. Landfill Mining in India

In 1997, the excavation and reuse of decomposed refuse from Deonar dump site in Mumbai, India was reported by Manfred Scheu and Bhattacharya. The excavation was carried out manually in a portion which was 4 to 12 years old and the soil fraction, formed by the decomposition of the biodegradable matter was separated from the rest of the waste by screening. The screened soil was then bagged and taken off the site, leaving the rest of the waste behind at the site itself.

The reclaimed soil was mixed with cow dung, dolomite, gypsum and neem cake (the residue after the oil is extracted from the neem seeds) and sold as a mixed fertilizer (Dumpsite Rehabilitation and Landfill Mining, Asian Regional Research Program on Environment Technology (ARRPET), Kurien, J. et al, 2004). The product was marketed in an appealing fashion stating various benefits of the product to yield and soil improvement.

#### 4. CONCLUSION

Based on the above discussion it can be inferred that landfill mining is more resource efficient in terms of utilizing the deposited refuse and land reclamation, as the other technologies typically bury all the deposited refuse forever in place, and the land is lost too. Moreover, landfill mining also provides a permanent remediation of the open dump sites which are potent sources of pollution and can contaminate the surrounding environment to very dire outcomes. For the same end, it becomes of high importance to study the waste composition of the Indian cities, and the dump sites, as the first step to ascertaining the feasibility of landfill mining operations on a conceptual level.

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# Environmental Restoration and Ecological Engineering

Sarthak Patel<sup>1</sup> and Neha Tiwari<sup>2</sup>

<sup>1</sup>Maharaja Agrasen College University Of Delhi, Delhi

<sup>2</sup>Saheed Rajguru College Of Applied Sciences For Women University Of Delhi, Delhi

E-mail: <sup>1</sup>sarthakpatelmac@gmail.com, <sup>2</sup>neha.manish95@gmail.com

**Abstract**—The contemporaneous age is gushing with technologies, yet the subject of safeguarding the natural resources continues to be a major concern. The needle of the clock is ticking towards the hour of “Technology with lesser disservice”. The quick-fix to the status quo is the cure of clean technology. These “cleaner” methods have been developed with the objective of being an advantage to the people on one hand and not sabotage the nature on the other. The resource which has turned out to be the “TIL scorpion venom in 21<sup>st</sup> century” calls for an instantaneous spotlight, this time a brighter one. An “ocean” of it is being flushed out repeatedly and we seldom care!!! This is the status of the clean usable water in this era of “sustainable evolution”.

Apparently the facts and figures of a survey reveal that an average household dissipates around 5.6 to 7.6 liters of water per minute for dish-washing while 3.8 liters of water each is exhausted with regard to teeth-brushing, face-washing and shaving purposes. The outrageous statistic is that the utmost part of it is foolishly flushed out to the drains. Water being wasted is wistful. A survey intended to specify the amount of water an average Indian household splurges out each day through and through the flush lead us to the idea of reusing the water outletted through the basins for the same.

usage. The idea is to outlet the waters from the basin to reach the flushes. Other sorts of reusable water sources can also have their “second innings” in the flush. This uncomplicated scheme when put into use thoughtfully could prove wonder some.

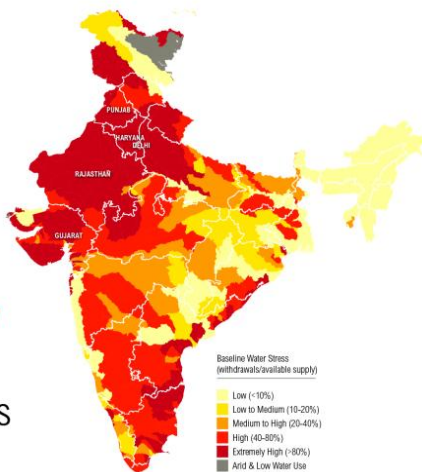
## 1. INTRODUCTION

The pivot resource, Water is also encircled in the endangered collection. The globe of the earth having a major part of it colored blue contradicts with the fact that millions of people can't even have water enough to drink.

The same is shown in the map below:

While the amount of clean usable water on the planet remains more or less the same, the population has detonated. The availability and access to clean potable water is the goal line. Availability, that implies that the sufficient amount of water on earth must be conserved and also the three R's must be put into practice to have appropriate amount for each one's need. Accessibility emphasizes on water being available to the person who needs it, in the form she needs it and in a quality that satisfies the individual. Access and bereaving underlie most water judgments.

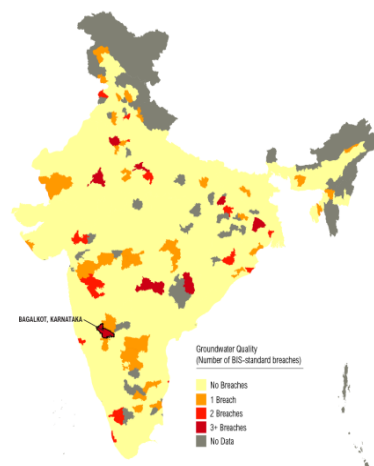
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The research basically has its foundation laid on the gallons of water recklessly depleted that could instead be put to proper and prolonged

The figure above makes us face the harsh actuality that the needle of the clock is ticking towards the hour of “Technology with lesser disservice”. The quick-fix to the status quo is the cure of clean technology. These “cleaner” methods are developed with the objective of being an advantage to the people on one hand and not sabotage the nature on the other. The earth and all that it owns is for the interest of all the creatures dwelling on it. This power in turn passes onto us the liability to use these judiciously. It not only plays a vital role in human survival, nourishment and health but also is a must for sanitation. The resource which has turned to be the “TIL scorpion venom in 21<sup>st</sup> century” calls for an instantaneous spotlight and this time a brighter one.

## 2. RESEARCH INVOLVED

H<sub>2</sub>O is a significantly strong pillar for an economy to flourish. Facts say that the water crisis is the Number 1 global risk based on impact to society (as a measure of devastation), and the Number 8 global risk based on likelihood (likelihood of occurring within 10 years) as announced by the World Economic Forum, January 2015. About one in every nine peoples lacks access to clean drinkable water, that takes it to the count of around 750 million people in the world. . If we exist, we need to have access to clean water for the sake of the existence to continue. The water that we drink today has been formed at the time when the dinosaurs were an actuality i.e. millions and millions of years ago. While some flush the fresh water, others die of gulping the contaminated one It seems as abundant as the air we breathe but the outer side of the window bewrays that it isn't that profuse. Letting the same to flow off uselessly is an extravagance. An “ocean” of it is being flushed out every day and we seldom care!!! This is the status of drink worthy water in this era of “sustainable evolution”. The data of water consumption was presented by the United Nations' Research and gave us the outcome that the freshwater consumption has tripled in the past fifty years and the demand for freshwater is increasing by 64 thousand liters. Moreover the amount of water wasted every year is around **2,797,482 billion liters**

Apparently the facts and figures of a survey reveal that an average household dissipates around 5.6 to 7.6 liters of water per minute for dish-washing while 3.8 liters of water each is exhausted with regard to teeth-brushing, face-washing and shaving purposes. The outrageous statistic is that the utmost part of it is foolishly dumped out to the drains. The average amount of water used in a flush has varied over time. Over the years, the total amount of water drained per flush has gone drastically down .Former toilets from the 1950s used eight gallons per flush. Currently, an average toilet manufactured today uses about 1.5 gallons per flush. Surveys also bring to our notice that an average person flushes atleast five times a day. Having done the math, We just say “Water being wasted is wistful”. They aptly say “You never know the worth of water until the well runs dry” . Similarly unless the scarcity of it begins to affect us directly, we can't abscribe the

prominence of the buckets of drops we let go in vain. A fact to be marked here is there isn't a need to make potable waters flow through the flushes; they can make use of water previously used by other sources.

## 3. OTHER ASPECTS

Not only the waters from the hand basins could be reused and thus the fresh water consumption by flushes could be reduced significantly, water from ROs, laundry, showers etc. could too be put to use. Figures show that an average shower uses almost 70-120 liters of freshwater. Another significant consumption is in laundry, 53-97 liters per load is used. Reverse osmosis systems use an approximate amount of 7 to 11 liters of tap water so as to produce 3.7 liters of pure drinking water. Such large amounts of water being dumped is stressful.



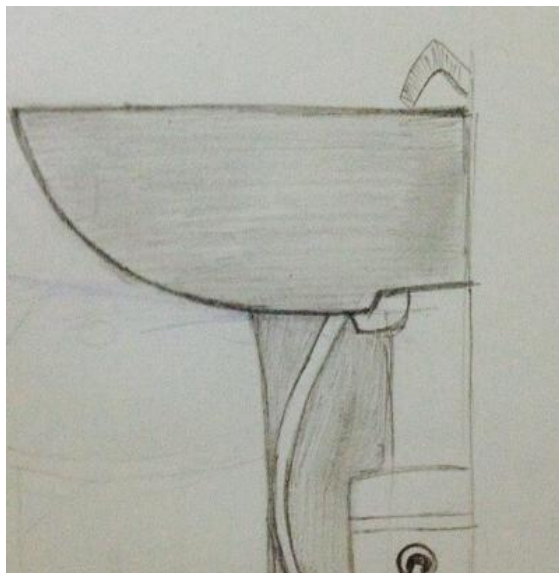
The water used for the purpose of showers, for instance, after usage becomes grey water which is clearly not synonymous to “waste water”. Our research model prioritizes to re-utilize this grey water from baths, dishwashers, faucets, showers, washing machines and letting it fill the toilet flushes which in turn saves the water wasted in that fraction as well. Isn't that a approach infallible for this age of the fast and the furious?

## 4. PROPOSED SOLUTION

One might not recognize grey water as an explication to the prevalent paucity but the exploration done on our part might bias your beliefs. It is an unpopular and abhorred approach to aqua conservancy. A survey intended to determine the amount of water an average Indian household splurges out each day through and through the flush lead us to the idea of reusing the water outletted through the basins for the same. The highest amount of water being dumped this way gives us a way out to conserve the most. The ground idea is that of reusing the waters drained from hand basins; however we can utilize water from the showers, baths, laundry and other grey water sources. An average person generates roughly 92.5 liters of grey water per day. The model that we have proposed through this particular research of ours is one consisting of drainage

pipes from all grey water originators connected to the flush tank. The partially clean water from these sources could be used as it is for the purpose to be served by flushes instead of pure clean water flown out recklessly.

The model looks like the figure as drawn below:



## 5. PRACTICAL APPLICATION

To divert grey water so as to rehash it, the pipes from all possible grey water origins must be affixed to the flush tank and this design must be laid upon the planning and manufacture of a new project. The research basically has its foundation laid on the gallons of water recklessly depleted that could instead be put to proper and prolonged usage. The idea is to outlet the waters from the basin to reach the flushes. Other sorts of reusable water sources can also have their “second innings” in the flush. Another example of the implementation of the scheme could be utilization of water from the ROs to serve the same. These uncomplicated ideas when put into use thoughtfully could prove wondrous.

## 6. CONCLUSION

Save to swig is the solitary solution to the cause. Water has always proved its prominence; it's time to acknowledge the same. There is no other doing other than “flush of a time” that dumps nearly 6 liters of sheer clear H<sub>2</sub>O in such a meager period of time. If we crave to assure water availability to the upcoming generations then we must ponder twice before we flush it all out. Water, Waste and Waste water, all three are separated by a thin line which might have been darkened by our research. Major scarcity of water scares us with the threat of death. The admitted apophthegm of “If it's yellow let it mellow” must be practiced in the coetaneous chronology.

Let's not drain the reason of our being out of the flush carelessly.

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# A Study of Active Packaging (AP) Technology on Banana Fruit

Ritu Yadav<sup>1</sup>, Aradhita Ray<sup>2</sup> and B.S. Khatkar<sup>3</sup>

<sup>1,2,3</sup>Guru Jambheshwar University of Science and Technology, Hisar, Haryana  
E-mail: <sup>1</sup>rituraoft@gmail.com, <sup>2</sup>dhitaray@gmail.com, <sup>3</sup>bskhatkar@yahoo.co.in

**Abstract**—Active packaging (AP) treatments (ethylene, moisture, Oxygen and Carbon dioxide scavengers along with an antimicrobial chitosan coating) were formulated in our laboratory and applied on whole banana fruits stored at room ( $30\pm 2^\circ\text{C}$ ) as well as refrigeration ( $5\pm 1^\circ\text{C}$ ) temperatures for 9 and 15 days respectively. Fresh and mature banana fruits were packed in LDPE with AP treatments with an objective to reduce the post harvest losses and preserve the storage life of the commodity. The fruits were analyzed for physico chemical parameters such as weight loss (%), moisture content (%), titratable acidity (%), ascorbic acid (mg/100g),  $\text{O}_2$  (%),  $\text{CO}_2$  (%),  $\text{C}_2\text{H}_4$  ( $\mu\text{l C}_2\text{H}_4/\text{h/kg}$ ). The results revealed that chitosan coating was found most effective followed by ethylene and moisture scavenging treatments in extending the shelf life of banana under room temperature but at refrigeration storage only chitosan coating treatment showed and proved better in reducing softness and retaining quality parameters. Hence, it can be concluded that active packaging technology has great potential for future development in reducing the postharvest losses and to prolong the shelf life of the horticultural produce.

**Keywords:** Active packaging, chitosan coating, scavengers, physico chemical parameters, treatments.

## 1. INTRODUCTION

India has emerged as the second largest producer of fruits and vegetables in the world only next to China, and in terms of total area and production our country is designated as “fruit and vegetable basket” of the world. Presently, India is producing around 88.977 million tonnes of fruits and 162.89 million tonnes of vegetables under a vast area of 7.216 and 9.396 million hectares, respectively [7]. Fruits are perishable and very liable to transport damage that consequently leads to deterioration in quality and wastage. In India, over 30 per cent of the total produce is wasted due to spoilage. Hence, there is an urgent need to develop technologies to overcome post-harvest losses of fruits [19]. In the present study active packaging (AP) technology applied to fresh fruits can provide an alternative way to control and extend quality and shelf-life during storage. Active or smart packaging techniques are proposed for better quality retention and shelf life extension of fruits and vegetables. The term ‘active’ reflects to perform some role other than providing some inert barrier to external conditions. “Active packaging (AP) is an innovative concept

that can be defined as a mode of packaging in which the package, the product and the environment interact to prolong the shelf life or enhance safety or sensory properties, while maintaining nutritional quality of the product” [18]. Five treatments oxygen scavenger, carbon dioxide scavenger, moisture scavenger, ethylene scavenger and chitosan based antimicrobial coating were selected under active packaging concept. This study discusses the effect of AP treatments on the quality of banana fruit stored at  $5\pm 1^\circ\text{C}$  refrigeration and  $30\pm 2^\circ\text{C}$  ambient temperature.

## 2. MATERIAL AND METHODS

### 2.1. Treatments of Fruits

**2.1.1. Oxygen scavenger.** 100g Iron powder based oxygen scavenger was prepared by selecting the following chemical materials i.e. 40g Iron powder, 30g magnesium sulphate ( $\text{MgSO}_4$ ), 20g sodium chloride ( $\text{NaCl}$ ) and 10g silica gel and all the chemical ingredients were mixed well with spatula.

**2.1.2. Carbon dioxide scavenger.** 100g activated charcoal based carbon dioxide scavenger was prepared by properly mixing of 80g activated charcoal and 20g silica gel with spatula by maintaining the ratio of 8:2.

**2.1.3. Moisture scavenger/ absorber.** For 100 g of moisture scavenger only silica gel was taken.

**2.1.4. Ethylene scavenger.** Potassium permanganate based ethylene scavenger was prepared by dipping 96g silica gel powder (AR grade) in 4 per cent  $\text{KMnO}_4$  (100 ml) solution for the preparation of 100g ethylene scavenger. The homogenous mixture was kept at  $28\text{-}30^\circ\text{C}$  temperature for 48 hrs. in hot air oven. Dark purple coloured ethylene scavenger powder was prepared and was packed in LDPE pouches for further use.

**2.1.1.1. Sachet Preparation.** Sachet was prepared by selecting high density woven fabric (100 gauge) which was permeable to gases but impermeable to active packaging ingredients, it was cut into 8 x 4 cm with scissors and 2 sides were sealed by using an electronic form, fill and seal machine. 4 x 4 cm size of each sachet was prepared with one side



remained open for incorporating the prepared scavengers and packed in LDPE pouches for further use.

**2.1.1.2. Filling of prepared scavengers inside sachet.** 5g dried scavenger granules of O<sub>2</sub>, CO<sub>2</sub>, moisture and ethylene scavengers were weighed and filled in sachet (4 x 4 cm) prepared from gas permeable high density woven fabric but impermeable to sachet ingredients and heat-sealed by using an electronic form, fill and seal machine and packed in LDPE pouches for further use.

**2.1.5. Chitosan based antimicrobial coating.** Chitosan (Sigma Chemical Co.) coating solution was prepared by dissolving 2g chitosan powder (correspond to 2 per cent) and volume made to 100 ml by 1 per cent acetic acid solution in which 0.4 ml glycerol was added as a plasticizer with continuous hand stirring from glass rod for approximately 30 minutes, until the whole chitosan powder was dissolved. The prepared solution was then de-gassed by using vacuum pump to avoid bubbling in the solution and before application the solution was kept undisturbed at 5±1°C for 24 hours.

## 2.2. Packaging of fruits

Fresh and mature banana fruits purchased from the local market, after washing and disinfecting the fruits and 150-250 g of samples were taken in LDPE bags. Further, sealing was done after incorporating the prepared sachets of particular scavengers. Chitosan coating solution was applied with brush and left for 5-10 min for surface drying and treated samples were stored at (5±1°C) refrigeration (RT) and (30±2°C) ambient temperature (AT). The fruits were analyzed after every 3<sup>rd</sup> day at room temperature and every 5<sup>th</sup> day at refrigeration temperature stored for a period of 9 days and 15 days respectively.

## 2.3. Physico chemical parameters

Physiological Loss in weight (PLW) was determined by the difference in initial and final weight readings. Moisture content was determined by following the standard method of AOAC [2]. Total acids were estimated by the method of Ranganna [15]. Ascorbic acid was determined by procedure detailed by AOAC [1].

**2.3.1. Oxygen and Carbon dioxide concentration.** The head space gas concentration was observed using Gas analyzer fitted with chromosorb column and thermal conductivity detector (TCD). The rate was expressed as per cent (%).

**2.3.2. Ethylene concentration.** Ethylene concentration was determined by the procedure adopted by Banks [3] by using gas chromatograph (Netel) fitted with chromosorb101 column and FID. The flow rate of carrier gas (nitrogen) was 29 ml/min, oven temperature 180°C, injector and detector temperature 200°C. Results were expressed as µl C<sub>2</sub>H<sub>4</sub>/Kg/hr fruit.

## 2.4. Statistical Analysis

The data was subjected to statistical analysis of variance using SAS (version 9.1). A significance level of 0.5 was chosen. Factors namely ethylene scavenger, O<sub>2</sub> scavenger, CO<sub>2</sub> scavenger, moisture scavenger, antimicrobial film and storage duration were selected or the study as factorial arrangements in Completely Randomized Design (CRD). Each mean value presented in the tables is the average of three replications.

## 3. RESULTS AND DISCUSSION

The results regarding changes in physico-chemical parameters are presented in the Figures 1-7.

### 3.1. Physiological loss in weight (PLW)

Fig. 1.(a,b) express the observations regarding the changes in PLW in banana at refrigeration and ambient temperature, recorded lower PLW (0.69 and 0.83%) for control samples than all the scavengers. Highest PLW value was observed for banana samples treated with moisture scavenger (2.03 and 1.30%) followed by ethylene scavenger (1.94 and 1.30%) and minimum PLW (0.33 and 0.61%) was found in chitosan coated samples at RT and AT on 15th and 9th day of storage respectively.

Highest PLW was observed in intact fruits may be due to high transpirational and respiratory substrate losses at ambient temperature. However the magnitude of losses was lower at low temperature and it may be due to reduced metabolic activities and evapotranspirational losses. Among the treatments of AP, chitosan coated fruits showed minimum weight loss throughout storage period, whereas, fruit samples showed maximum PLW when treated with ethylene scavenger followed by moisture scavenger followed by O<sub>2</sub> and CO<sub>2</sub> scavenger as these scavengers possess the tendency to absorb moisture from the fruit surface and utilized in the chemical reactions, so all the scavengers happened to absorb water during storage. At ambient temperature, among all the treatments minimum reduction in PLW was observed in coated fruits. The results obtained in the present investigation are in accordance with previously reported results by increase in PLW with increasing duration of storage but the PLW was lower in coated samples than the control in mango fruit stored at ambient conditions (20-30°C and 70-90% RH), Giri *et al.* [6]. Further, Lin and Zhao [13] observed that edible coatings provide an effective barrier to oxygen, carbon dioxide and water vapour transmission thus helping to alleviate the problem of moisture loss.

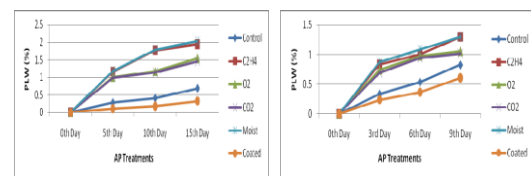


Fig. 1: Effect of Active Packaging on PLW (%) of banana at RT and AT

### 3.2. Moisture content

Observations regarding the effect of AP on moisture content (%) of banana fruits during storage at refrigeration and ambient temperature are presented in Fig. 2.(a,b) respectively. Initial moisture content for banana was recorded 73.29%. Moisture content of all banana samples was found increasing with advancement of storage period both at RT and AT. Maximum increase i.e. 80.33% and 80% for control samples and minimum increase 77.37% and 77.33% in chitosan coated samples was observed at RT and AT on 15th and 9th day of storage, respectively. Total transfer of moisture from peel to pulp and enzymatic degradation of starch and other molecules might be the possible reason of increase in moisture content in banana fruit. The higher moisture percentage in banana was recorded at refrigerated temperature (RT) as compared with ambient temperature (AT) because low temperature storage is responsible for chilling injury in banana and thereby deterioration of banana fruit and among the AP treatments, chitosan coated fruits showed the best results with respect to chilling injury. It reduced the increase in moisture content in banana and recorded to be 77.4% at RT and 77.3% at AT on the final day of storage and remain acceptable. The highest moisture content in banana fruit was observed in the control samples followed by the samples treated with CO<sub>2</sub> scavenger > O<sub>2</sub> scavenger > moisture scavenger > ethylene scavenger > chitosan coating. AP treatments significantly ( $p < 0.05$ ) reduced the movement of moisture from peel to pulp with the advancement of storage. The increase in moisture content with increase in storage duration was reported by Lizada *et al.* [14] who found that water is withdrawn from peel to pulp, consequently, water content decreases in the peel but not in the pulp during ripening. Our results are also in agreement with the findings of Sarode and Tayade, [16] who also reported the similar behaviour of moisture content i.e. movement of moisture from peel to pulp in banana fruit when stored at 32°C.

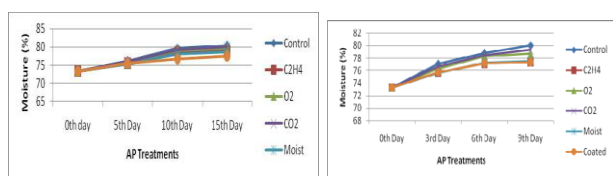


Fig. 2: Effect of Active Packaging on moisture content (%) of banana at RT and AT

### 3.3. Titratable acidity

Observations regarding the effect of AP on titratable acidity (%) of banana fruits at refrigeration and ambient temperature storage conditions are presented in Fig. 3.(a,b) respectively. Initial titratable acidity for banana was 0.23%. A gradual decline in titratable acidity was observed with the advancement of storage period in all the treatments of AP at refrigeration as well as ambient temperature. Maximum retention (0.163 and 0.161%) was observed in chitosan coated

samples followed by samples treated with ethylene scavenger (0.162 and 1.161%), moisture scavenger (0.159 and 0.161%), O<sub>2</sub> scavenger (0.157 and 0.154%), CO<sub>2</sub> scavenger (0.153 and 0.147%) and minimum (0.150 and 0.122%) was observed in control samples at RT and AT on 15th and 9th day of storage respectively. AP treatments except CO<sub>2</sub> significantly retained acidity at RT whereas, at AT all AP treatments significantly retained the acidity ( $p < 0.05$ ). The control fruit samples had minimum acidity at the end of the storage at RT and AT. However the magnitude of reduction in acidity was lower at low temperature than AT storage conditions that attributed to lower rate of ripening. The progressive decrease in acidity could be due to conversion of acids into sugars during ripening process. Among AP treatments, chitosan coated samples were found to be effective in maintaining higher acidity i.e. it significantly decreased the reduction in acidity at RT at final day of storage whereas, AP treatments except CO<sub>2</sub> scavenger significantly retained the acidity in all the fruits at AT. This is supported by Castro *et al.* [5] who observed that the rate of reduction in acidity in coated fruits compared to uncoated fruits is low due to restriction of oxygen availability that leads to reduced respiration rate. Further, Jiang *et al.* [10] also reported the effect of chitosan coatings on litchi fruit and found that titratable acidity decreased during storage.

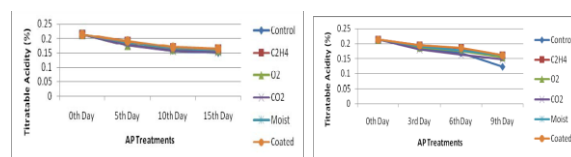


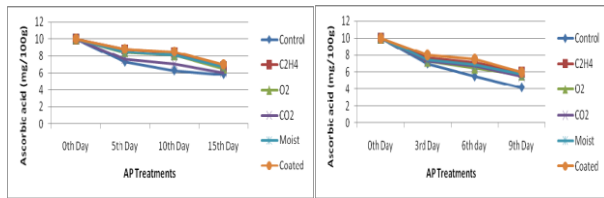
Fig. 3: Effect of Active Packaging on titratable acidity (%) of banana at RT and AT

### 3.4. Ascorbic acid

The observations regarding the effect of active packaging on ascorbic acid content (mg/100g) of banana fruits are presented in Fig. 4.(a,b) for banana at RT and AT respectively. The initial ascorbic acid content was (10.0 mg/100g) in banana. AP significantly ( $p < 0.05$ ) maintained the ascorbic acid content during storage. A gradual reduction in ascorbic acid was observed in all treatments under active packaging for the entire fruit samples and minimum was observed in control fruit samples at RT and AT, however the magnitude was low at RT. The results obtained in the present investigation are in accordance with the previously reported results of Ishaq *et al.* [8] who investigated the physico-chemical characteristics of apricot fruit at 28 to 30°C and 60-63% RH and observed the decreasing trend of ascorbic acid with passage of time, might be due to the conversion of dehydroascorbic acid to diketogluconic acid by oxidation. However, among AP treatments maximum retention of ascorbic acid was observed in fruits coated with chitosan and treated with ethylene scavenger followed by moisture, O<sub>2</sub> and CO<sub>2</sub> scavengers on the final day of storage under both the storage temperatures. The reason for high ascorbic acid content in chitosan coated



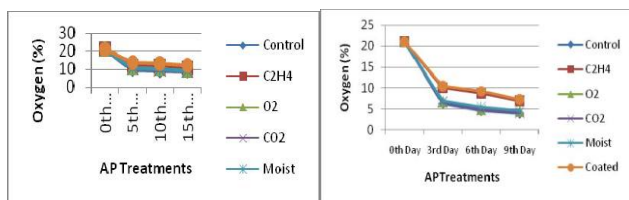
fruits can be attributed to slow ripening rate of treated fruits. Srinivasa *et al.* [17] observed that coatings prevent transfer of gases between the fruit and atmosphere and served as a protective layer that control the permeability of O<sub>2</sub> and O<sub>2</sub> and therefore, prevent the oxidation of vitamin C by hindering the fruit's exposure to oxygen, altering enzymatic activity and slowing the respiration process.



**Fig. 4: Effect of Active Packaging on ascorbic acid (mg/100g) of banana at RT and AT**

**3.5. Oxygen and Carbon dioxide**

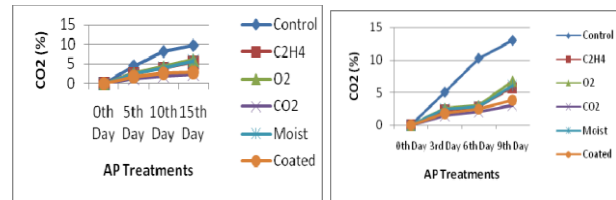
The headspace O<sub>2</sub> and CO<sub>2</sub> (%) levels in all the fruit packages were analyzed using gas analyzer and the observations regarding O<sub>2</sub> concentration are presented in Fig. 5.(a,b) for banana whereas; the observations regarding CO<sub>2</sub> concentration for are presented in Fig. 6.(a,b) for banana. The initial concentration of O<sub>2</sub> was 21% and CO<sub>2</sub> was 0.03%. Maximum retention of O<sub>2</sub> concentration (12.20 and 7.37%) was observed in chitosan coated banana samples followed by samples treated with ethylene scavenger (10.57 and 6.93%), moisture scavenger (9.23 and 4.60%), O<sub>2</sub> scavenger (9.13 and 4.50%), CO<sub>2</sub> scavenger (9.13 and 4.17%) and lowest (8.47 and 4.03%) in control samples at RT and AT on 15th and 9th day of storage respectively. AP treatments significantly (p<0.05) maintained the O<sub>2</sub> concentration at RT whereas; AP treatments except CO<sub>2</sub> and O<sub>2</sub> scavengers significantly maintained the O<sub>2</sub> concentration at AT.



**Fig. 5: Effect of Active Packaging on O<sub>2</sub> (%) of banana at RT and AT**

Lowest CO<sub>2</sub> concentration (2.43 and 3.07%) in banana samples treated with CO<sub>2</sub> scavenger followed by chitosan coated samples (2.90 and 3.87%), ethylene scavenger (5.40 and 5.80%), moisture scavenger (5.77 and 6.05%), O<sub>2</sub> scavenger (6.07 and 6.78%) and highest (9.7 and 12.97%) was observed in control samples at RT and AT on 15th and 9th day of storage respectively. AP significantly (p<0.05) reduce the increase in CO<sub>2</sub> concentration at RT and AT. In general, level of O<sub>2</sub> and CO<sub>2</sub> showed a gradual decrease and increase respectively. From the results it can be concluded that control

samples had highest CO<sub>2</sub> concentration than the samples treated with AP treatments. All the AP treatments especially chitosan coated samples followed by ethylene and moisture scavengers delay ripening by the modification of gases and thereby significantly reduce (p < 0.05) the rate of respiration at both the storage temperatures. However, the magnitude was low at RT (low temperature). Our results are in accordance with Jiang and Li [11] who studied the effect of chitosan coating on fruits and concluded that chitosan coating may form a protective barrier on the fruit surface which reduces the availability of O<sub>2</sub>, and delays ripening in fruits. Furthermore, chitosan coating can also reduce the internal O<sub>2</sub> concentration in treated fruits and so produce low CO<sub>2</sub> and ethylene concentration. Further, Baez-Sanudo *et al.* [4] evaluated the effects of 1-methyl cyclopropene and chitosan based edible coating on banana fruits during storage of 8 days at 22°C, 85% RH and found that treated fruits showed a lower rate of respiration than control fruits.

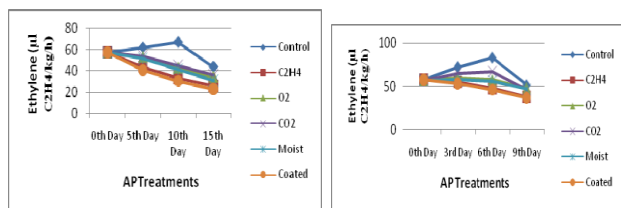


**Fig. 6: Effect of Active Packaging on CO<sub>2</sub> (%) of banana at RT and AT**

**3.6. Ethylene**

The observations regarding the effect of AP treatments on ethylene concentration of banana fruit are presented in Fig. 7.(a,b) at RT and AT. At 0 day initial ethylene concentration (57.5 µl C<sub>2</sub>H<sub>4</sub>/kg/h) was reported. Chitosan coated samples exhibited minimum ethylene concentration (22.91 and 36.77 µl C<sub>2</sub>H<sub>4</sub>/kg/h) followed by samples treated with ethylene scavenger (25.53 and 37.85 µl C<sub>2</sub>H<sub>4</sub>/kg/h), moisture scavenger (31.17 and 46.71 µl C<sub>2</sub>H<sub>4</sub>/kg/h), O<sub>2</sub> scavenger (34.15 and 48.09 µl C<sub>2</sub>H<sub>4</sub>/kg/h), CO<sub>2</sub> scavenger (35.91 and 46.25 µl C<sub>2</sub>H<sub>4</sub>/kg/h) and maximum concentration (43.67 and 51.56 µl C<sub>2</sub>H<sub>4</sub>/kg/h) was observed in control samples at RT and AT on 15th and 9th day of storage respectively. AP significantly (p<0.05) reduce the increase in ethylene concentration at RT and AT. The highest ethylene concentration was observed in control of all fruit samples and the lowest was recorded in chitosan coated fruits followed by ethylene and moisture scavenger. AP treatments can delay the ripening process in fruits by slowing down or trapping the ethylene production. Maximum delay in respiration rate as well as ethylene evolution was observed under AP treatments at both the storage conditions so, there was delay in the climacteric rise of CO<sub>2</sub> production in AP treated fruits. Jayaraman and Raju [9] prepared three matrices (based on silica gel, alumina and limestone and cement) impregnated with KMnO<sub>4</sub>, studied their effects on fresh fruits and vegetables at 10°C and

ambient storage and concluded that alumina-limestone based formulation increased the overall extension of shelf-life from 3-8 days. Kudachikar *et al.* [12] found that banana packed with LDPE film in combination of ethylene adsorbent stored under 13°C extended the shelf-life upto 42 days.



**Fig. 7: Effect of Active Packaging on ethylene ( $\mu\text{l C}_2\text{H}_4/\text{kg/h}$ ) of banana at RT and AT**

#### 4. CONCLUSION

The results reveal that among AP treatments applied on whole banana fruits, chitosan based coating was most effective for all whole fruits in providing improved storage life and quality of the fruits, followed by ethylene, moisture, O<sub>2</sub> and CO<sub>2</sub> scavenging treatments at refrigeration ( $5\pm 1^\circ\text{C}$ ) and ambient temperature ( $30\pm 2^\circ\text{C}$ ). At refrigeration temperature chitosan coated banana samples showed best results and proved better in reducing the softness and chilling injury whereas, other treatments were not found so effective it possibly may be due to chitosan coating is acting as a barrier between the fruit peel and the refrigerated condition due to which the chilling injury may be reduced in the treated samples as compared to control. Chitosan coated fruits followed by samples treated with ethylene, moisture, O<sub>2</sub> and CO<sub>2</sub> scavengers showed lower weight loss (%), retained higher moisture content, TSS, total sugar contents and CO<sub>2</sub> concentration and higher retention of titratable acidity, ascorbic acid, pectin, ethylene and O<sub>2</sub> concentration.

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# Formula Optimization of Active Packaging Treatments for Research

Ritu Yadav<sup>1</sup>, Aradhita Ray<sup>2</sup> and B.S. Khatkar<sup>3</sup>

Guru Jambheshwar University of Science and Technology, Hisar, Haryana  
E-mail: rituraoft@gmail.com

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**Abstract**—Active packaging (AP) is one of the innovative food packaging concepts that have been introduced as a response to the continuous changes in current consumer and market demands. Very little work has been done on AP technology of fruits and vegetables in our country therefore; five AP treatments were chosen and formulated for laboratory study to reduce the post harvest losses. The main aim of the present study was to extend the shelf life of fruits and vegetables while maintaining its nutritional quality with minimum changes in terms of physico-chemical, microbial and organoleptic parameters with storage. Oxygen scavenger (iron powder), carbon dioxide scavenger (activated charcoal) ethylene scavenger (potassium permanganate), moisture scavenger (silica gel), chitosan based coating were selected under Active packaging concept. Their formulations were standardised and best formulation was finalised for research as per the results obtained. Prepared scavengers were filled into the sachet (4x4 cm) made from gas permeable high density woven fabric.

**Keywords:** Active packaging, formulation, fruits, sachet, scavengers.

## 1. INTRODUCTION

India has emerged as the second largest producer of fruits and vegetables in the world only next to China, and in terms of total area and production our country is designated as “fruit and vegetable basket” of the world. In recent years, the major driving forces for innovation in food packaging technology is perhaps due to the increase in consumer demand for lightly processed food. In the present study, Active or smart packaging techniques are proposed for better quality retention and shelf life extension of fruits and vegetables. The term ‘active’ reflects to perform some role other than providing an inert barrier to external conditions. According to Suppakul [1] “Active packaging (AP) is an innovative concept that can be defined as a mode of packaging in which the package, the product and the environment interact to prolong the shelf-life or enhance safety or sensory properties, while maintaining nutritional quality of the product” (Active packaging systems can be classified into active scavenging systems (absorbers) and active-releasing systems (emitters). Vermeiren [2] suggested that scavenging systems remove undesired compounds such as oxygen, excessive water, ethylene, carbon dioxide, taints and other specific food compounds whereas releasing systems actively add compounds to the packaged

food such as carbon dioxide, water, antioxidants or preservatives. Both absorbing and releasing systems aim at extending shelf-life and/or improving food quality.

Limited research has been done on Active Packaging (AP) of fruits and vegetables in our country. Therefore, the present work has been undertaken to optimize the AP treatments for fresh fruits and vegetables in prolonging the shelf life while maintaining its nutritional quality with minimum changes in terms of physico-chemical, microbial and organoleptic parameters with storage. In order to achieve this broad objective, Five treatments, oxygen scavenger, carbon dioxide scavenger, moisture scavenger, ethylene scavenger and chitosan based antimicrobial coating were selected under active packaging concept. Their formulations were standardized as per the results given, and best formulation was finalised for studying the effect of AP on fresh fruits and vegetables. These scavengers were prepared and filled into the sachet. The formulations/preparation of AP treatments is described under material and methods heading.

## 2. MATERIALS AND METHODS

### 2.1 Formula optimization of active packaging treatments

Formulation of four types of scavengers and an antimicrobial film forming solution are described below: For the preparation of O<sub>2</sub> and CO<sub>2</sub> scavengers, four different types of formulations were tried as given in Table 1-2. and the best one was selected on the basis of absorption of O<sub>2</sub> and CO<sub>2</sub> gases, respectively. O<sub>2</sub> and CO<sub>2</sub> concentrations were checked by placing 5g of sachet of these scavengers in two 100 ml air tight glass jars fitted with a rubber septum. O<sub>2</sub> and CO<sub>2</sub> concentrations were periodically analyzed by using headspace analyzer.

#### 2.1.1 Oxygen scavenger

Table 1. describes the formulation of O<sub>2</sub> scavenger based on iron powder which was used in the present study. For this four different type of formulation ratios (2:1:1:1, 4:3:1:2, 4:3:2:1 and 4:2:3:1) were tried and finally 100g of oxygen scavenger was prepared by dry mixing of 40g Iron powder with 30g magnesium sulphate, 20g sodium chloride and 10g silica gel

by maintaining the ratio of 4:3:2:1, this concentration for O<sub>2</sub> scavenger was chosen on the basis of oxygen reduction by this formulation. As shown in the given Table 1. the selected concentration of O<sub>2</sub> scavenger, reduces the O<sub>2</sub> concentration from 21 to 19.96 per cent when analyzed after 2 days. On storage the grey coloured iron based oxygen scavenger changed into rusty colour due to oxidation.

**Table 1: Formulation of oxygen scavenger**

Material taken	O <sub>2</sub> (%) present	Formulation selected
Iron Powder +MgSO <sub>4</sub> +NaCl +Silica gel (40+20+20+20)	20.03	Iron powder+MgSO <sub>4</sub> +NaCl+Silica gel (40+30+20+10)
Iron Powder +MgSO <sub>4</sub> +NaCl +Silica gel (40+30+10+20)	20.06	
Iron Powder +MgSO <sub>4</sub> +NaCl +Silica gel (40+30+20+10)	19.96	
Iron Powder +MgSO <sub>4</sub> +NaCl +Silica gel (40+20+30+10)	20.06	

### 2.1.2 Carbon dioxide scavenger

Table 2. describes the formulation of CO<sub>2</sub> scavenger based on activated charcoal, for this four types of formulations were tried by using activated charcoal as main ingredient and silica gel in different concentration ratios (1:0, 9:1, 8:2 and 7:3) and finally for 100g of CO<sub>2</sub> scavenger was prepared by mixing 80g activated charcoal with 20g silica gel by maintaining the ratio of 8:2. This concentration was selected on the basis of CO<sub>2</sub> absorption as shown in the given Table 2. The selected concentration of CO<sub>2</sub> scavenger reduces the CO<sub>2</sub> concentration from 0.03 to 0.016 per cent when measured after 4 days.

**Table 2: Formulation of carbon dioxide scavenger**

Material taken	CO <sub>2</sub> (%) present	Formulation selected
Activated charcoal (100g)	0.02	Activated charcoal+silica gel (80+20)
Activated charcoal+silica gel (90+10g)	0.02	
Activated charcoal+silica gel (80+20g)	0.016	
Activated charcoal+silica gel (70+30g)	0.023	

### 2.3 Moisture scavenger

Silica gel acts as an effective desiccant therefore; it was used as such for the application of moisture scavenger as a treatment under active packaging (AP) for fruits and vegetables and is given in Table 3. Each sachet of 5g moisture scavenger was prepared for this purpose.

**Table 3: Formulation of moisture scavenger**

Material taken	Formulation selected
Silica gel (100g)	Silica gel

### 2.4. Ethylene Scavenger

Ethylene scavenger was prepared in the laboratory. Five different formulations of ethylene scavenger based on potassium permanganate were prepared, by impregnating 96g sand with 100 ml of 4% KMnO<sub>4</sub> solution, 96g jamuna ret with 100 ml of 4% KMnO<sub>4</sub> solution, 96g limestone with 100 ml of 4% KMnO<sub>4</sub> solution, 96g plaster of paris with 100 ml of 4% KMnO<sub>4</sub> and 96g silica gel with 4% KMnO<sub>4</sub>, mixed and allowed to dry at 28-30°C temperature in hot air oven, packed in LDPE pouches and allowed to store at room temperature for two weeks. Ethylene scavenger selection was done on the basis of colour changes from bright purple (initial colour) to brown (oxidised colour) when stored for 15 days as described in Table 4. For the preparation of 100g ethylene scavenger, the formulation based on mixing of silica gel with 4% KMnO<sub>4</sub> was selected for further study.

**Table 4: Formulation of ethylene scavenger**

Material taken	Colour (visual basis)	Formulation selected
Sand + 4% KMnO <sub>4</sub>	Light Brown	Silica gel + 4% KMnO <sub>4</sub>
Jamuna Ret + 4% KMnO <sub>4</sub>	Light Brown	
Limestone + 4% KMnO <sub>4</sub>	Light Purple	
Plaster of Paris + 4% KMnO <sub>4</sub>	Light Purple	
Silica gel + 4% KMnO <sub>4</sub>	Bright Purple	

#### 2.4.1. Selection of sachet material

Fresh produce packages have addressed their perceived primary problem by employing package structures that have high gas permeability by value of their polymeric structure, gauge, surface to volume ratio or mineral or other fill. Table 5. describes that the selection criteria of the sachet material for the preparation of sachets of various treatments like C<sub>2</sub>H<sub>4</sub> scavenger, O<sub>2</sub> scavenger, CO<sub>2</sub> scavenger and moisture scavenger. As 100 gauge (thick) sachet material (woven fabric) was selected on the basis of permeability to gases but impermeable to the sachet ingredients.

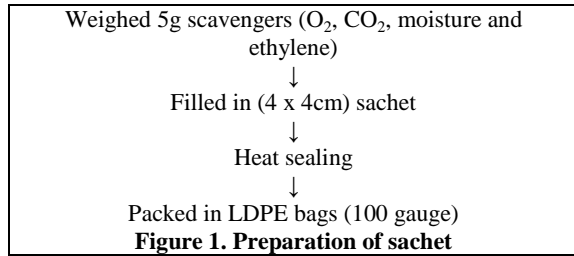
**Table 5: Selection of sachet material**

Material taken	Material selected
40 gauge	100 gauge
60 gauge	
70 gauge	
80 gauge	
90 gauge	
100 gauge	

**2.4.2. Sachet preparation:** Sachet was prepared by selecting high density woven fabric (100 gauge) which was permeable to gases but impermeable to active packaging ingredients, it was cut into 8 x 4 cm with scissors and 2 sides were sealed by

using an electronic form, fill and seal machine. 4 x 4 cm size of each sachet was prepared with one side remained open for incorporating the prepared scavengers and packed in LDPE pouches for further use.

**2.4.3. Filling of prepared scavengers inside sachet:** 5g dried scavenger granules of O<sub>2</sub>, CO<sub>2</sub>, moisture and ethylene scavengers were weighed and filled in sachet (4 x 4 cm) prepared from gas permeable high density woven fabric but impermeable to sachet ingredients and heat-sealed by using an electronic form, fill and seal machine and packed in LDPE pouches for further use.



**2.5. Antimicrobial film/coating**

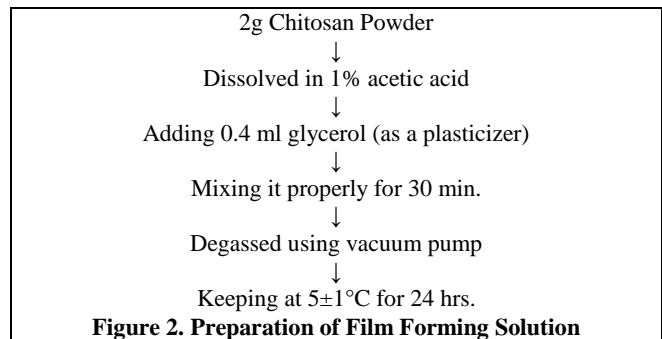
To control undesirable microorganisms in foods, antimicrobial substances can be incorporated or coated. The application of chitosan based edible films to the fresh fruits and vegetables has been one method of extending its shelf-life by slowing down its metabolic processes. For the preparation of film forming solution (FFS) based on chitosan, four different concentrations were taken as described in Table 5. and FFSs were prepared by dissolving 2g chitosan in 100 ml of 1% acetic acid solution, secondly, 2g chitosan was dissolved in 1% acetic acid with the addition of 0.2 ml glycerol as a plasticizer, third concentration was prepared by dissolving 2g of chitosan in 100 ml of 1% acetic acid solution with the addition of 0.4 ml of glycerol and fourth concentration was prepared by dissolving 2g chitosan powder in 100 ml of 1% acetic acid with the addition of 0.6 ml glycerol. Glycerol as plasticizer was added to film forming solution to reduce brittleness, increase toughness, strength, tear and impact resistance and impart flexibility. Usually, the addition of a plasticizer increases the permeability of gas, water vapour and solute and decreases the tensile strength of the films.

All the film forming solutions that were prepared by above mentioned concentrations were allowed to stand for atleast 30 min. for complete dissolution of chitosan, the prepared solutions were degassed under vacuum for the removal of bubbles. 20 ml solution was pipetted out from each of the concentration, put it in the petri plates and placed in refrigerated conditions (6±1°C) at least for 48 hrs. After this the prepared films were automatically peeled off from the

surface of petri plates. Finally, third concentration was selected because on the basis of the formation of film it showed best results. The films prepared from this formulation were transparent and good in quality in terms of colour, smoothness and extensibility whereas, the films produced from the first, second and fourth concentration were pale yellow in colour and had rough or gritty surface, pale yellow with gritty surface but less than first one and transparent, smooth but less elastic in nature, respectively.

**Table 5: Formulation of antimicrobial film forming solution**

Material taken	Observation of films	Formulation selected
2g chitosan+1% acetic acid	Pale yellow with Rough surface	2g chitosan+1% acetic acid + 20% glycerol (20% chitosan powder)
2g chitosan+1% acetic acid+0.2ml glycerol	Brittle and less Rough	
2g chitosan +1% acetic acid+0.4ml glycerol	Transparent and smooth surface	
2g chitosan+1% acetic acid+0.6ml glycerol	Transparent, smooth but not flexible	



**3. CONCLUSION**

Best formulations for different treatments under active packaging namely oxygen, carbon dioxide, moisture, ethylene scavengers and film forming solution for coating were optimized for further study.

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# Ruthenium Heteroleptic Complex Immobilized to SBA-15 for Visible Light Driven Oxidative Cyanation of Aromatic Tertiary Amines

Chetan Joshi<sup>1</sup>, Pawan Kumar<sup>2</sup> and Suman L. Jaina<sup>3</sup>

<sup>1,2,3</sup>Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun-248005, India;  
E-mail: <sup>1</sup>chetanjoshi019@gmail.com

**Abstract**—The direct oxidative cyanation of C-H bonds in tertiary amines to give corresponding  $\alpha$ -aminonitriles has gained importance in recent years, prominently due to highly useful and versatile intermediates which find wide application in the construction of biologically active nitrogen compounds such as alkaloids. Dual reactivity shown by these bifunctional organic compounds, as nucleophilic addition provides an easy access to other compounds such as  $\alpha$ -amino aldehydes, ketones and  $\beta$ -amino alcohols.<sup>1</sup> Considering the huge importance of these compounds in nature, scientists have dedicated their research in the development of clean and environmentally benign methods for the transformation of amines into the corresponding  $\alpha$ -functionalized compounds. Sunlight is an inexhaustible source of energy and can provide activation energy required for the organic transformation.<sup>2</sup> Due to this, scientific community has been attracted towards the solar light harvesting for the organic transformations which is considered most economical source of energy. Till date, most of the work was carried out on semiconductor photocatalysis which works by generating electrons and hole pairs but in the semiconductor photocatalysis conversion efficiency and quantum yield was found low in visible light due to wide band gap. Metal complexes due to their visible light absorption efficiency are considered to be suitable catalysts for visible light driven organic transformations. But, the main challenge associated with these redox catalysts is their homogenous nature which restricts their recyclability. However, immobilisation of these homogenous metal complexes on photoactive supports like graphene, carbon nitride, SBA-15 etc. makes them recyclable as well increase their catalytic performance. Herein, we report a new microwave synthesized heteroleptic ruthenium previously synthesized by our group and characterised by <sup>1</sup>H and <sup>13</sup>C NMR, ESI-HR-MS and UV-Vis spectroscopy. The synthesized catalyst was immobilized on highly mesoporous SBA-15 material as efficient photoredox catalyst for oxidative cyanation of wide range of tertiary amines to corresponding  $\alpha$ -aminonitriles via C-H activation and characterized by FTIR, TGA, XRD, ICP-AES, BET, CHNS, UV-Vis etc. The catalytic activity of the photocatalyst was tested for the oxidative cyanation of various tertiary amines under visible light irradiation. The developed catalytic system yields  $\alpha$ -aminonitriles from corresponding amines in excellent yields. Due to the heterogenization of the synthesized catalyst on the photoactive support, it can be recovered and reused for further reactions without much loss in the activity.

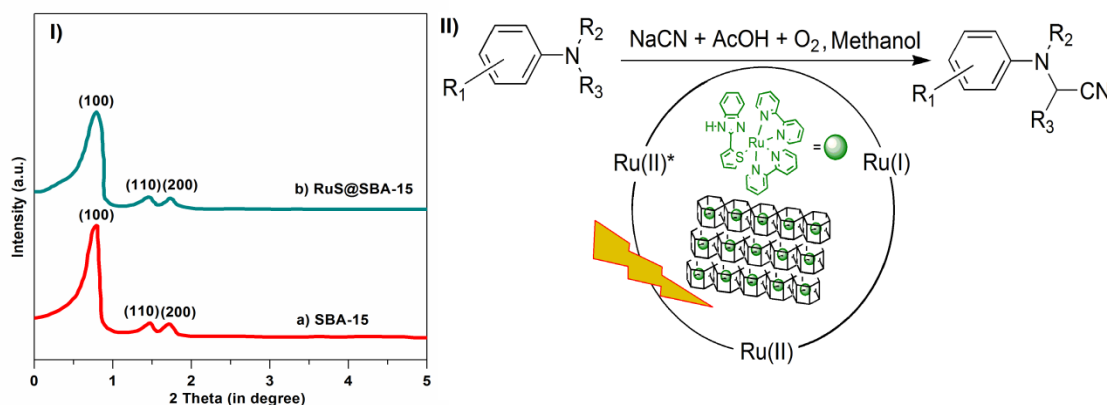


Fig. 1 I): Short angle XRD diffraction pattern of a) SBA-15 b) RuS@SBA-15 II) Schematics of visible light induced photocyanation of tertiary amines.

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# Sustainable Management Systems for Improving Soils and Environmental Quality

Sandeep Kumar

Department of Plant Science, South Dakota State University, Brookings, South Dakota (SD)  
E-mail: [sandeep.kumar@sdstate.edu](mailto:sandeep.kumar@sdstate.edu)

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**Abstract**—Intensive tillage, imbalanced use of fertilizers and pesticides in cropland, heavy metal contaminants from industrialeffluents, and accelerated soil erosion are the primary causes of soil and water quality impairments in watersheds located within the Midwest USA. A total of more than 1.7 billion tons of soil are eroded by water and wind each year from the US croplands. The other major challenges that reduce soil and water quality include intensivegrazing, land use change, deforestation and drainage problems. Several conservation-effective practices have been identified and tested. Important among these are conservation tillage systems, biochar amendment, cover crops, and diversification of cropping systems. These practices can improve soil organic carbon (SOC), reduce erosion, and improve the quality of soil and water resources. In Ohio, a study showed that SOC improved with usage of 47 years of no-till ( $18.5 \text{ g kg}^{-1}$ ) farming compared plow-till ( $13.9 \text{ g kg}^{-1}$ ) systems in the top 20 cm depth under poorly-drained soils. Similarly, SOC under long-term (49 years) NT ( $16.4 \text{ g kg}^{-1}$ ) systems increased by 30% compared to plow-till ( $11.8 \text{ g kg}^{-1}$ ) in well drained soils of Ohio. Cover crops are also beneficial in improving soil quality and reducing transport of agricultural chemicals in water runoff. Crop rotation with leguminous cover crops reduce N inputs, and can extract plant-available N which was unused by the previous crop, thus saving additional synthetic nitrogen fertilizer use, and reducing N losses. Cover crops used in high corn residue removal improved SOC ( $27 \text{ g kg}^{-1}$ ) by 6% compared to that without cover crops ( $25.4 \text{ g kg}^{-1}$ ) in South Dakota. Conducting field experiments for assessment of long-term benefits of conservation systems is expensive and takes significant time to show impacts on soils and water quality improvement. Further, these conservation practices are site-specific and one-size-fits-all recommendations for these practices are inappropriate because of varying soil type, management and climate. Therefore, models are very useful tools for simulating the long-term impacts of best management practices for improving soil and environmental quality under diverse environmental conditions. For instance, a hydrologic modeling study conducted in Missouri shows that rotational grazing reduces surface runoff by 10% compared to intensive grazing. This study also concludes that installing agroforestry buffers at the edge of grazed watersheds (with no cattle access) reduces surface runoff by 57% and sediments by 49% compared to the watersheds without buffers. Another modeling study conducted in Ohio showed that use of cover crop in corn-soybean rotation under no-till and plow-till showed 37 and 19% lower mean annual runoff, respectively, compared to continuous corn under same tillage systems. In conclusion, modifications in current conventional soil and management systems, diversifications of cropping systems and an integrated research and modeling approach is needed for improving crop productivity, SOC, and water quality.

# Highly Active Cobalt Doped Meso-ceria for Visible Light Assisted base Free Oxidation of Mercaptanes to Disulfides

Pawan Kumar<sup>1</sup>, Deepak Chauhan<sup>2</sup>, Chetan Joshi<sup>3</sup>, Nitin Labhsetwar<sup>4</sup>,  
Sudip K. Ganguly<sup>5</sup>, and Suman L. Jain<sup>6</sup>

<sup>1,3,6</sup>Chemical Sciences Division, CSIR-Indian Institute of Petroleum, Dehradun 248005, India

<sup>2,5</sup>Refining Technology Division CSIR-Indian Institute of Petroleum, Dehradun 248005, India

<sup>4</sup>Environmental Materials Division, CSIR-National Environmental Engineering

Research Institute (CSIR-NEERI), Nagpur-440020, India

E-mail: <sup>1</sup>choudhary.2486pawan@yahoo.in

**Abstract**—Oxidation of thiols to disulfides is immensely important because this not only remove thiols from petroleum products but also extracted thiols can be used in synthetic industries. Many catalytic systems like conventional oxidants such as manganese dioxide, dichromates, chlorochromates, etc., other catalytic systems like cobalt, manganese, copper, vanadium, cerium, and nickel based catalysts have been reported for the aerobic oxidation of thiols into disulfides. Visible light initiated organic transformation has attracted scientific community for the development of green and sustainable catalytic system. Semiconductor like  $\text{TiO}_2$ ,  $\text{CeO}_2$  etc. can may be applied for this purpose because of their electron transferring ability. Meso  $\text{CeO}_2$  is good in the sense of its good visible light absorption pattern. But high electron hole pair recombination rate. Most of doping methods use wet surface imprgnation methods that show leaching of metals from the surface of semiconductors catalyst. In this work we have developed a new method of cobalt, nitrogen and carbon doping on the surface of  $\text{CeO}_2$ . The synthesized catalyst was charecterized with various techniques like SEM, TEM, FTIR, UV, XPS, ICP-AES, CHNS, BET, DT-TGA etc that confirm the well synthesis of catalyst. The developed catalyst was used for visible light driven thiols oxidation to disulfides. Various thiols from  $\text{C}_2$  to  $\text{C}_{12}$  were checked for the photooxidation. All thiols was oxidized to disulfides within 5 hours. Further we have checked photocatalytic activity of catalyst for the oxidation of thiols in kerosene having premixed dococene thiols as model substrate for simulating conditions of sulfur containing thiols. It was found that catalyst was well functioning in this medium too. For confirming that developed catalyst was robust enough we have carried out recycling experiment and after four recycling there were no significant loss in activity of catalyst was found.

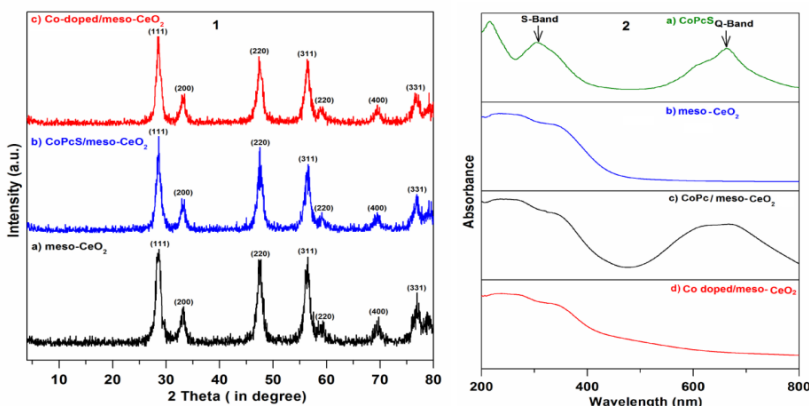


Fig: 1: a) XRD diffraction pattern of a) meso-CeO<sub>2</sub> b) CoPcS/meso-CeO<sub>2</sub> and c) Co-doped/meso CeO<sub>2</sub> and 2. a) UV-Vis spectra of CoPcS b) meso-CeO<sub>2</sub> c) CoPcS/meso-CeO<sub>2</sub> d) Co-doped/meso CeO<sub>2</sub>

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# Density, Viscosity and Ultrasonic Velocity of Aqueous Hemoglobin Solution in Presence of Different Sugars

Saeeda Naqvi<sup>1\*</sup> and Naseem Ahmed<sup>2</sup>

<sup>1</sup>Chemistry Section, Women's College, Aligarh Muslim University, Aligarh – 202002, India

<sup>2</sup>Chemistry Department, Government PG College, Rajouri, Jammu India

E-mail: <sup>1</sup>[saeedaznaqvi@gmail.com](mailto:saeedaznaqvi@gmail.com)

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**Abstract**—*In the present work, the density, viscosity and ultrasonic velocity values of aqueous solutions of hemoglobin in presence of different sugars, viz., D-glucose, D(-)fructose, sucrose and maltose have been measured as functions of concentration of sugars (keeping the concentration of aqueous hemoglobin solution constant) and temperature have been measured and various parameters have been derived for the said system in an attempt to understand the stabilization of hemoglobin in presence of different sugars.*

**Keywords:** *hemoglobin, sugars, density, viscosity and ultrasonic velocity.*

# Polypyrrole-zirconium(IV)SelenoiodateCation Exchange Nanocomposite: Synthesis, Characterization and its Application as a Formaldehyde Sensor

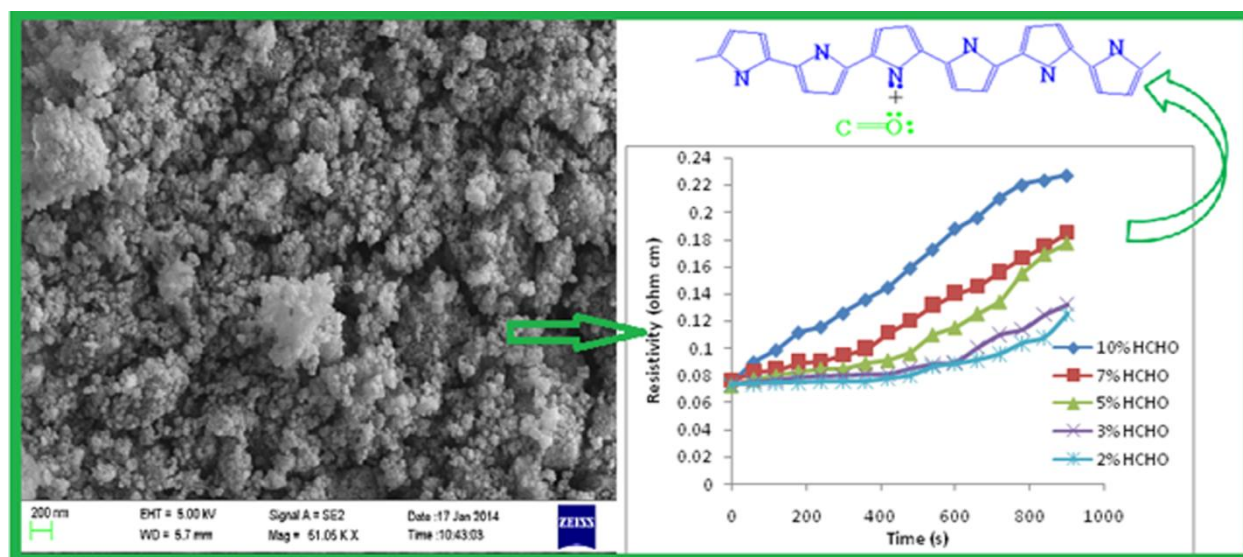
NidaAlam

\*Analytical and Polymer Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002 (UP), India.

\*Environmental Research Laboratory, Department of Applied Chemistry, Faculty of Engineering and Technology, Aligarh Muslim University, Aligarh 202002 (UP), India  
E-mail: [alamnidz@gmail.com](mailto:alamnidz@gmail.com)

**Abstract**—Polypyrrole-zirconium(IV)selenoiodate (PPy/ZSI) cation exchange nanocomposite has been synthesized by chemical oxidative polymerization of polypyrrole in the presence of inorganic entity zirconium(IV)selenoiodate by sol-gel method. The formation of PPy/ZSI nanocomposite was characterized by fourier transform infra-red spectroscopy (FTIR), x-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive x-ray (EDX), transmission electron microscopy (TEM) and thermogravimetric analysis (TGA). The ion exchange capacity of the nanocomposite was found to be  $2.49 \text{ meqg}^{-1}$ . Also, its electrical conductivity was determined by using a four-in-line probe and was measured to be  $0.436 \text{ S cm}^{-1}$ . The nanocomposite showed appreciable isothermal stability till  $130^\circ\text{C}$  in terms of DC electrical conductivity retention under ambient condition. In addition, the cation exchange nanocomposite based sensor for detection of formaldehyde vapors was fabricated at room temperature. It was revealed that the resistivity of the nanocomposite increases on exposure to higher percent concentration of formaldehyde at room temperature ( $25^\circ\text{C}$ ), also the sensor exhibited good reversible response towards formaldehyde vapors ranging from 5-7%. The present study may serve as a basis for designing other smart materials for formaldehyde sensors.

**Keywords:** Nanocomposite, polypyrrole, conductivity, formaldehyde, sensing.



# District Heating Techniques for Reduction of Carbon Footprint

Rishikaysh Pardessi

(T.Y.Mech Student) Department of Mechanical Engineering  
Sinhgad College of Engineering, Vadgaon, Pune  
E-mail: rishikaysh21@gmail.com

**Abstract**—A carbon footprint is “the amount of carbon dioxide or other carbon compounds emitted into the atmosphere by the activities of an individual, company or country”. Typically a carbon footprint is measured over a specific amount of time such as one year. There are so many things that we all do on a daily basis that have an effect on our environment. i.e. The energy we use in our homes. How many lights and electronic devices we have plugged in and running at once, our home thermostat and our laundry habits create our carbon footprints.

District heating system can provide cost-effective and low-carbon energy to local populations, such as space heating in winter and year-round hot/cold water; this is also associated with electricity generation in combined-heat-and-power systems. In India including the Renewable Heat Incentive, aim to increase the amount of energy from such sources; including new installations, as well as extending/upgrading existing distributed energy schemes. Country should have award-winning district energy network, incorporating city-wide heat distribution. This paper aimed to demonstrate the opportunities for expansions to this through geographical information systems of the heat demands in the city. ‘Heat maps’ can be reproduced; locating existing and emerging heat sources and sinks. A number of current and emerging heat sources are also discovered – potential suppliers of thermal energy to the above-defined heat sinks. From these ‘heatzones’ an expansion to the existing network could be possible to identified and the infrastructure planned for each development.

## 1. INTRODUCTION

District heating system(DHS) offers excellent opportunities for achieving the twin goals of saving energy and reducing carbon footprint. It is an extremely flexible technology which can make use of any fuel including the utilization of waste energy, renewables and, most significantly, the application of combined heat and power (CHP). It is by means of these integrated solutions that very substantial progress towards environmental targets, such as those emerging from the Kyoto commitment, can be made.

While designing and implementing the conversion of buildings to chilled water based district cooling systems, for example, the distribution of chilled water at a temperature between 1°C and 4°C and a maximum pressure of 1.0 MPa (150 psig). These data will be applicable to a variety of

building types, including residential, commercial, institutional and industrial.

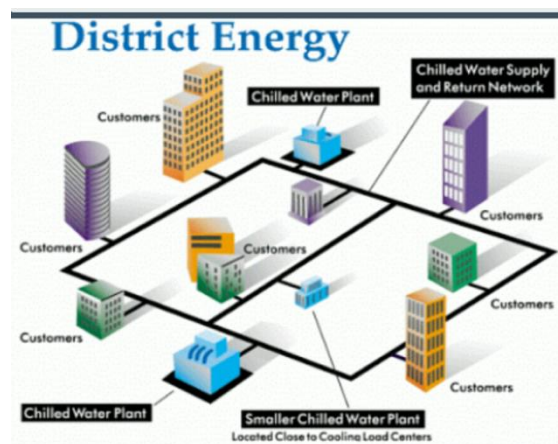


Fig. 1: District heat energy Distribution

The conversion procedures is concentrate on the types of conditions most likely to be found in cold weather countries i.e. centralized chilled water district cooling systems, service to a variety of building sizes and types, applicable to both new and existing primarily on larger buildings. It's always possible the indirect and direct connection between the district chilled water and building systems.

To provide practical advice on converting buildings in the most cost-effective manner while ensuring that the system is technically sound and provides reliable and efficient cooling using a district cooling system. Design and installation.

In all times, the engineer should always consult the district cooling utility. The design engineer shall be responsible for the detailed design, specification, and final selection of all equipment, systems, and components.

Form water retention technologies. Byusing DHS rather than a traditional rooftop mechanical room, space is made for water retention technologies that could not otherwise be built. By reducing the amount of water flowing from a building site, municipalities reduce the risk of sewer overflows and can

reduce the infrastructure required for storm water containment. Lastly, a DHS produces thermal energy on a large scale and is technology neutral. The nature of DHS allows for fuel diversity and flexibility. Should the cost of any one type of fuel increase dramatically in price, DHS have the ability to switch sources with minimal investment. DHS will allow municipalities to ensure their communities will be able to maintain reasonable fuel costs and a high standard of living. None of these economic benefits are included in current feasibility analyses yet they can be substantial. If these factors were included, the economic case for DHS would be made quite easily and communities could then benefit from the reduced carbon footprint for their heating and cooling.

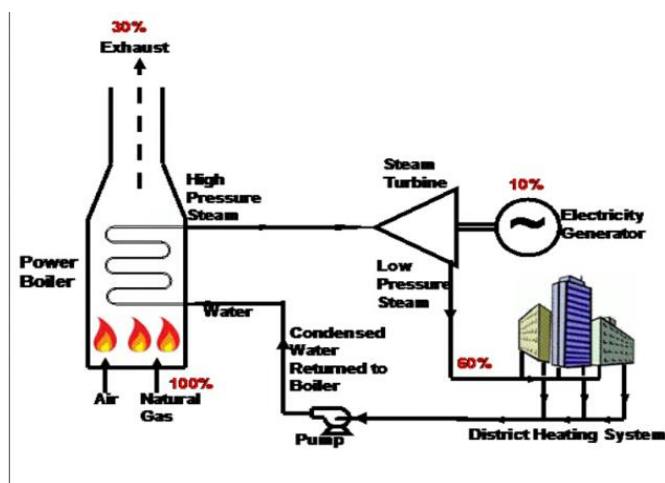


Fig. 2: Schematic diagram of DHS

## 2. ENERGY SECURITY AND REDUCING INFRASTRUCTURE COSTS IN POWER GENERATION AND WATER MANAGEMENT

A District heating system (DHS) has the potential to help governments, at all levels, reduce operating and infrastructure costs. These opportunities, however, are often left unexplored. In a free market environment, DHS development will only take place with a strong business case for a DHS Utility and its customer base. By recognizing and crediting the cost savings that a DHS affords governments, the business case for DHS would be strengthened and help policy makers to take advantage of the eco-efficiencies these systems provide.

Governments are averse to providing financial or human capital to support the private sector without a reasonable expectation of socio-economic benefits for taxpayers. While these capital intensive systems do not necessarily need government support to be economically viable, returns are often marginally below acceptable levels for investors. By helping the private sector breach the risk/reward threshold, municipalities could reduce their own operating costs by millions of dollars with minimal investment and risk.

To realize the additional benefits of DHS, it is crucial to understand what district energy systems are, the current business case for district energy, and the economic and environmental opportunities that are complementary to government objectives such as: power generation, storm water management, energy security, and economic growth.

District energy is a technical solution for providing the thermal energy used for conditioning indoor spaces. DHS are generally comprised of three major components:

- A common or shared energy generating facility referred to as a central energy plant or community energy centre,
- A system of interconnected pipes that link the energy centre(s) to multiple buildings referred to as a distribution piping system or thermal grid,

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- A thermal interface at the customer building referred to as a customer substation or energy transfer station.

In the case of district heating system, hot water (or steam) is transported through a system of pipes and delivered to the customer buildings for space heating and domestic water heating. The heat energy carried in the fluid is extracted by the building's systems and the cooled water is returned to the central energy centre, in a closed loop piping system, where it is reheated for redistribution. Similarly with district cooling, chilled water is pumped through a network of pipes and the cooling energy is extracted by the building for air conditioning or process cooling and then the warmed water is returned to the plant to be cooled again.

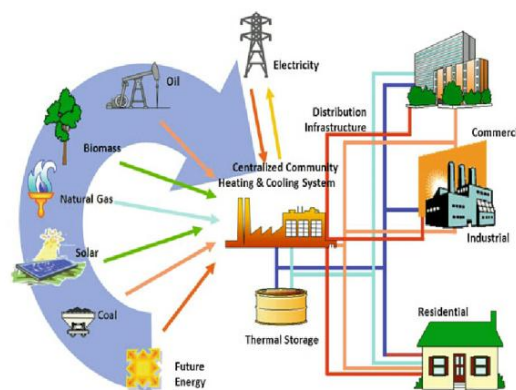


Fig. 3: illustrates that DHS is not technology specific

Multiple or single fuel sources and/or technologies can be employed including but not limited to: absorption chillers, ambient cooling, deep lake water cooling, combined heat and power, biomass incineration, waste incineration, geothermal, and conventional boiler and chiller technologies.



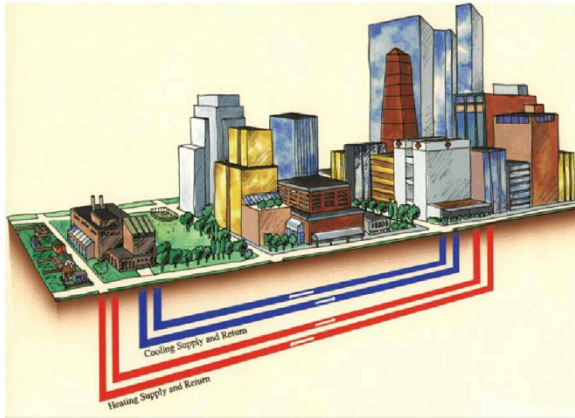


Fig. 4: illustrates how DHS typically works.

Pipes run underground bringing heating and cooling energy to buildings from a central energy plant.

Economies of scale and advancements in technology have enabled DHS to achieve greater efficiencies than individual building systems. Serving multiple buildings from a common facility allows for large scale systems to be built that can accommodate state-of-the-art technologies in heating and cooling. For example, individual buildings could not cost effectively make use of natural lake water cooling or Combined Heat and Power (CHP). Using natural sources of cooling or waste heat sources from manufacturing or electricity generation can reduce energy consumption for the production of thermal energy to near zero. In addition, economies of scale in DHS enable the efficient use of conventional equipment by:

- Having purpose built facilities that are actively maintained and operated
- Aggregating thermal loads from multiple and a variety of types of buildings so that equipment can be run optimally with less part loading.

Thermal energy generating equipment such as boilers and chillers operate most efficiently at a single load factor (Chan 2002). This concept is analogous to the fuel efficiency of a car, reaching optimal fuel economy between 50 and 80 km/h (NRCAN 2012a, b). A car traveling outside of its 'sweet spot' will use more fuel per km travelled. Likewise, a boiler or chiller will use more energy for every unit of thermal heating or cooling when forced to operate above or below its 'sweet spot'. By having an aggregated load, a DHS can 'stage' its boilers and chillers by operating only the number required by while maintaining each in its efficiency 'sweet spot'.

The earliest DHS is dated as far back as the 1300s. The first known system distributed warm water through a series of wooden pipes in France. In 1877, the first commercial DHS was built in New York (CDEA 2011). DHS are not a new concept. Though widely embraced in Europe, DHS have not seen the How District Energy Systems can be used to Reduce

Infrastructure Costs 199 same rate of adoption in North America. Abundant and low cost energy supplies have reduced the urgency for conservation and innovation in thermal energy production. However, energy constraints, limited dollars, and environmental concerns are putting DHS on the public agenda. To address these concerns, policy makers can examine the synergistic opportunities that DHS can provide.

### 3. A CASE FOR DHS

A case for DHS fails to examine or value the economic and environmental benefit to other stakeholders such as industries, communities, and governments. The industry standard for determining the feasibility of investing in DHS is based solely on the economic benefit to both the building owner(s) (customers) and the DHS utility.

For the DHS Utility, the profitability of developing a DHS is evaluated by comparing the initial capital investment costs to the expected cash flow over the life of the system. Capital costs include the cost to build the DHS infrastructure: the energy centre, the distribution piping system, and the customer connections. Expenses are dictated by fuel, operating, maintenance, and administration costs. Revenue is based on a capacity charge to the customer as well as energy delivery charges. The price is dictated by the Business-As-Usual (BAU) cost to produce thermal energy for space heating, cooling, and domestic hot water. After a financial analysis, the DHS Utility decides if the business case for DHS passes the risk/reward threshold that the investor is willing to accept.

A similar economic analysis is performed by the building developer or owner comparing the price of the district energy service to the current (or estimated) capital and operating costs of providing building heating and cooling. The district energy service is priced competitively, equal to or below, the BAU model. The cost savings a building would realize by connecting to a DHS is comprised of some or all of the following:

- Reduction in initial and/or replacement capital cost for major mechanical equipment including cost of associated space, electrical installation, and auxiliaries
- Fuel costs (i.e. natural gas for heating, and electricity for cooling)
- Cost of water, sewer, and water treatment
- Equipment operating and maintenance cost, including yearly preventative maintenance and ongoing repair/overhaul costs
- Cost of labor, administration, and insurance
- Value of "freed up" roof space, greenhouse gas reduction, risk mitigation, and liability.

Three to opportunities are their respect to DHS benefits can be found in:

- Reduction in electrical generating capacity,
- Storm water management, and
- Improving energy security: risk mitigation and management.

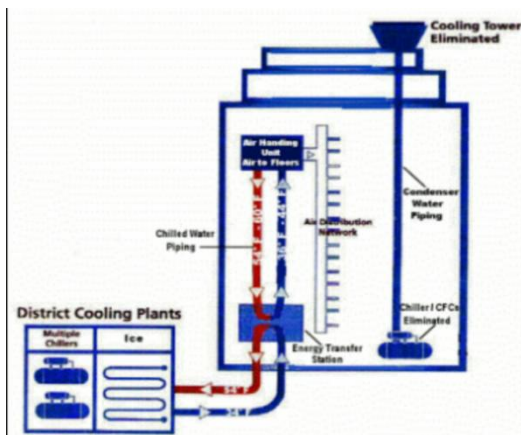
The important benefits listed above, may not be categorized as direct benefits to either the DHS Utility or the building owner, however, they are the only two parties paying for DHS development. Measuring and giving credit to the private sector for the positive contributions of DHS to the public sector, would help policy makers take advantage of synergistic eco-efficiencies.

**4. REDUCTION IN ELECTRICITY GENERATION**

**4.1 Eco-efficiency Opportunity**

In most countries, the electrical grid faces the most strain during the hottest days of the year due to the electricity requirements for air conditioning. Cooling loads, however, can vary substantially throughout the day and because the highest electricity demand comes in the summer time during the hottest time (IESO 2010), the greatest benefit from conservation efforts will come from reducing energy demand at that time.

1 kWh saved during peak time is more significant than one saved at night. Exacerbating the problem, line losses are higher during peak times than low usage times. When the electricity transmission and distribution systems get hotter, the loss can be substantially higher than the average. In Ontario, the variation ranges from 5 % during low usage times to 25 % during peak hours according to an Ontario Hydro study. Taking into account the total losses from generation to delivery, saving 1 kW during peak times can reduce generating requirements by 1.47 kW (Ontario Hydro 2007).



**Fig. 5: Shows particular buildings switched from running its own chillers to a DHS**

By reducing peak demand, the province can reduce its use of the less environmentally attractive resources that are called on when demand is high. In the long run, lower peak demand will mean less need for new generating facilities and transmission and distribution infrastructure

The electricity demand of a 30 story office tower for the year before the transition to district cooling and after. It is indicative of the savings that DHS could provide. The

Electrical load before and after conversion to DHS for a glass building demand in electricity drops by roughly one third at the time of switchover. Reducing electrical demand translates into fewer gas fired generating stations needing to be built in populated areas.

**2 Savings CostBenefits**

Electrically driven chillers for the most part generate more than 1 thermal unit of cooling energy for each unit of electricity. Rather than reference efficiencies in terms of percentages greater than 100, it is common practice to refer to chiller efficiencies in terms of Coefficient of Performance (COP). A fairly inefficient chiller with a COP of 3 produces 3 units of thermal energy for each unit of electrical energy. Assuming that chillers in the DHS on average can produce a COP of 5 (requiring 0.1 kWe of electricity per kWth) compared to a BAU COP of 3 (requiring 0.3 kWe of electricity per kWth) (mostly due to scale efficiencies) at peak times, each kilowatt thermal (kWth) of cooling demand translates to 0.2 kWe of electricity demand reduction.

If DHS utilities are able to capitalize on their size and generate and store chilled water at night (instead of producing it during the day), the peak time generation demand can reduce the cooling energy to effectively zero, saving 0.5 (kilowatt electrical) kWe for each kWth of cooling required. In the case of free cooling by snow, lake water, or other natural sources, the peak time savings are also on the order of 0.5 kWe for each kWth of cooling since in both cases of chill storage and free cooling, only pumping energy for the water is required.

Table 1 gives the possible load reductions.

For a contracted gas fired power plant.

**Table 1: Peak reductions cooling (at source)/kWthat generation source per kWth cooling due to DHS when compared to BAU**

Table 1 Peak reduction by District heating System	
Centrifugal chillers	0.1–0.3 kWe
Thermal storage	*0.5 kWe
Free Cooling	*0.5 kWe

Every MW of generation that can be avoided translates into significant savings.

**4.3 Environmental Benefits**

Reducing electricity use at peak times not only reduces the need to build more generating capacity, it potentially reduces carbon footprint and Greenhouse Gas (GHG) emissions.

Ontario, for example, uses a combination of nuclear and hydro power to satisfy the base load of electricity. As demand increases, the source of power tends to get dirtier.

As demand increases, carbon footprints and GHG emitting sources of generation come online. By using less energy during peak times (usually from noon to early evening), DHS can reduce CO<sub>2</sub>e, NO<sub>x</sub>, and SO<sub>x</sub> in the atmosphere

It is readily apparent that a base load is supplied by nuclear and hydro while natural gas

How District Energy Systems can be used to Reduce Infrastructure Costs

**Table 2: NO<sub>x</sub> and SO<sub>x</sub> output for various electricity generation forms (NRCAN GHGenius 2010) g/kWh**

	Coal	NG Boiler	NG Turbine	Nuclear	Hydro
NO <sub>x</sub>	2.64	0.59	0.56	0.00	0.00
SO <sub>x</sub>	4.96	0.01	0.01	0.00	0.00

Is the first choice for marginal requirements. As the demand increases, coal starts to come online as a last resort given how dirty it is.

Table 2 shows the difference in NO<sub>x</sub> and SO<sub>x</sub> output between different forms of electrical generation. Ontario still requires coal to meet its demand at peak times. Coal fired power plants produce nearly 3 g of NO<sub>x</sub> for each kWh of electricity and 5gSO<sub>x</sub> for each kWh of electricity. Conversely, nuclear and hydro do not add carbon footprint (during the operational phase of the life cycle). Using DHS to simply shift what time electricity is used for heating and cooling buildings could have a dramatic effect on pollutant emissions.

Although, studies have shown the correlation between NO<sub>x</sub>, and SO<sub>x</sub> with asthma and other respiratory illnesses (Lebowitz 1996; Detels et al. 1991), the cost savings from reducing emissions is difficult to calculate. Countries such as Canada, with government funded health care, can consider the cost savings associated with reducing the incidences of asthma and related respiratory illnesses as a bottom line benefit. A person with asthma in Ontario will on average cost the health care system twice what a person without the disease would cost (To 2007). If regulators and medical professionals can estimate the correlation between health care costs and the amount of carbon footprint in the air, policy makers can begin to understand the dollar value of preventative versus reactionary health care costs.

In the same way that atmospheric carbon footprint can be reduced, DHS can play a role helping countries meet GHG reduction targets. The authors conducted a study based on the electrical output in Ontario for 2009 and 2010;

**Table 3** shows that DHS could decrease GHG emissions by as much as 145 g of CO<sub>2</sub>e for each kWh of thermal cooling.

In many jurisdictions, there is no value assigned to GHG reduction. In these areas, DHS utilities and building owners receive no economic benefit for the reduction in GHGs that a DHS offers. Governments can encourage adoption of DHS by providing an incentive equal in value to reduction initiatives. Alternatively, a fee or tax on emissions could incentivize connection to DHS.

**Table 3: Cooling (IESO, NRCAN 2010)**

	Centrifugal chillers	Thermal storage	Free cooling
GHG reduction per kWh	67g	35-145g	145g

Putting a price tag on GHG emissions and carbon footprint reduction may not be popular in many jurisdictions but policy makers should recognize its merits. Deciding the value of each ton of GHGs reduced and applying that value to projects could spur innovation beyond DHS.

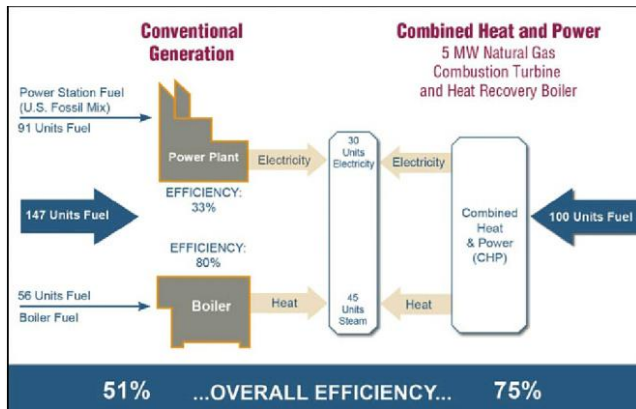
**5. ENERGY SECURITY:**

**Risk Mitigation and Management**

**5.1 Eco-efficiency Opportunity**

DHS provide governments an opportunity to protect the reliability of local energy systems through conservation, diversity, flexibility, and availability. The International Energy Agency (IEA) defines energy security as “the uninterrupted physical availability at a price which is affordable, while respecting environmental concerns.” With the growth of urban centers and the associated energy intensification required to provide essential services, governments are increasingly challenged to address issues of energy security. DHS can address factors, such as supply, price stability, and sustainability that contribute to greater energy security and independence.

The DHS thermal grid which connects energy producers to end-users aids in conservation efforts. This connection allows waste heat from industrial or power generating processes to be used for residential and commercial heating. By utilizing waste heat sources, DHS reduce the amount of fuel burned for space heating and improve the efficient use of fossil fuels.



**Fig. 6:** illustrates that using waste heat from conventional power production, a concept known as CHP, can increase system efficiency and reduce fuel input from 147 to 100 units, a 30 % reduction. It is estimated that 61 % (OEE 2008) of building energy usage in Canada is used for space heating and cooling and water heating; a 30 % reduction fuel used in buildings is substantial. Waste and renewable fuels are available for heating and since fossil fuels are finite, there is value to reserving this precious resource for applications that have no other alternative such as pharmaceuticals and medical devices and equipment.

DHS can expand the diversity of fuel types used for heating and cooling by taking advantage of local fuel sources that would otherwise remain unused. Fuels such as biomass (wood chips, sawdust, straw), geothermal, biogas, and municipal waste are difficult to manage on a small scale—largely due to handling issues. The availability of local fuel sources and the ability to use them reduces the reliance on supplies from countries or jurisdictions that may be adversely affected by war, politics, or natural disaster. According to Sandor Boyson, research professor and co-director of the Supply Chain Management Center, “the longer the supply chain, the more that can go wrong and the more it costs with high gas prices.”

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(University of Maryland, date unknown). In other words, a diverse fuel mix that incorporates local sources increases energy independence and reduces risk of supply interruptions and price instability.

The thermal grid and the centralized nature of energy production facilities allow DHS to support fuel switching and the implementation of state-of-the-art technologies. These qualities are referred to as fuel flexibility and technology flexibility; both improve the ability to optimize energy production in terms of cost and efficiency. The scale and centralized nature of DHS allow multiple fuel sources and/or technologies to be integrated at one location at a lower cost, than at many, in each individual building. In some cases

certain fuels and technologies cannot even be applied on an individual building scale.

## 5.2 Cost Savings

The risk of not addressing energy security is real and can have a significant impact on the economy. Costs can be examined from at least two perspectives:

- Cost of interrupted to fuel/energy supply
- Cost of the inflexible nature energy production.

The recent power outage in India of July 2012, the North-eastern Blackout of August 2003, and the North American Ice Storm of January 1998 are only a few reminders of our reliance on energy. An estimate of the economic impact of the North-eastern Blackout of 2003 is in the range of \$7.0 billion dollars (USD) from food spoilage, lost production, wages, etc. with the loss of 61,200 MW (ECLON

2004). Using the above figures, the economic impact of an energy supply interruption could be on the order of magnitude of \$114,000 (USD)/MW of electrical supply loss (over the outage period). A catastrophic failure, similar in duration, of the W.A.C. Bennett Dam in B.C. at 2,730 MW or the Adam Beck I and II (Niagara River) in Ontario at 2,278 MW can have an economic impact in the order of \$228 M (USD).

The value of mitigating energy (thermal and electrical) supply interruptions and pricing is difficult to estimate. As a gross estimate, municipalities could estimate the value of lost productivity as a function of the average GDP. This may help put into perspective the cost of each hour of unavailable electricity and thermal energy.

The inability of buildings to retrofit existing equipment to use alternate or renewable fuels or to implement more efficient technologies can reduce the competitiveness and robustness of an economy. Many industries, businesses (especially small ones), and households would encounter financial difficulties dealing with the consequences of a sharp increase in energy prices. Fluctuating energy prices can have a negative effect on many industries such as manufacturing, mining, transportation, forestry, and agriculture resulting in unemployment, loss of skilled labour and high paying jobs, as well as higher priced food and consumer goods resulting in a decreased standard of living

The value of being prepared for changes in the future, of being flexible, and of having a diversity of local fuel sources can be estimated by exploring the capital cost to modernize existing building heating and cooling systems for a group of buildings compared to a large scale DHS. Additional factors to examine can include depreciated building value and the exposure to utility cost fluctuations of relying on a single fuel source for example, electric baseboard heating).



**5.3 Environmental Benefits**

Retrofitting hundreds of small boilers to use waste wood, bio-fuels, or solar energy would be much more expensive than modifying a single energy centre. The ability to switch fuels in a cost-effective manner means a higher likelihood of space heating and cooling needs being met by renewable sources.

Oujé-Bougoumou, an early adopter of DHS in Canada has found that the presence of DHS has displaced conventional energy sources such as fossil fuel and raised community awareness to environmental issues (Ouje 2012).

Energy is integral to modern living and the impact of energy supply interruptions is real and tangible. Through conservation, diversity, and flexibility, DHS contribute to greater energy security and independence.

**6. BENEFITS BEYOND PRICE**

In evaluating eco-efficiency opportunities, in some cases, there are direct costs; Not all benefits have obvious or cost savings. For example reducing the incidence rate of asthma and other pollutant related diseases could reduce the burden on state funded health care systems but it is difficult to put a price tag on the value of a healthy person or improved quality of life. Important questions to ask when developing sustainability plans include:

- What is it worth to the city/town to avoid living next to an electricity generator?
- What is it worth of reducing air emissions? If a price cannot be put on health, can a price be put on net emissions?
- How much has it cost to the economy, historically, when the electricity grid fails? How much financial risk is the municipality willing to accept?

There are challenges to limiting evaluation metrics to only measurable cost but it does not diminish the value of considering externalities such as clean air and water, improved health, community engagement, and public opinion.

By reaching outside of the direct cost benefits and including ancillary benefits to the analysis, the authors hope to create a broader more accurate evaluation of DHS and the role it plays in reducing demands on energy infrastructure and consumption.

**7. RECOMMENDATIONS**

Municipal, regional, and federal governments should take advantage of the real dollar savings that DHS affords. This can only be done by identifying, understanding, and quantifying the costs and eco-efficiencies that DHS could save municipalities.

Table 4 opportunities and benefits

**Table 4: Eco-efficiency opportunities of DHS systems**

Eco-opportunity	Benefit	Metric/Key performance indicators
Electricity generation	Demand reduction	kW demandreduction/kW generating capacity reduction Air pollution reduction
Storm water reduction	Runoff reduction	\$/% reduction in mitigation Water pollution reduction
Economic risk mitigation	Electrical grid stability	% reduction of blackouts
	Energy price stability	Reduce volatility
	Fuel flexibility	Minimize time to convert primary fuel sources

carbon footprint reduction management %/\$ Electrical grid Energy price stability identified. The metrics and key performance indicators can be used as a guide for developing sound public policy surrounding DHS. Without strong public policy to lead the way, the full environmental benefits of DHS will be difficult to realize.

Beyond financial incentives or economics, the greatest hurdle to developing DHS, as in any business, is getting customers—without customer buildings, there can be no DHS development. Even with a business case, signing customers is challenging because the status quo or engrained industry practices are difficult to overcome. People are generally adverse to change current business practices, especially when a proven method is achieving good results. Exacerbating the problem, many buildings are built and developed by a separate entity which owns and operates the building leaving little incentive to seek out efficiencies, reduce GHG emissions, or address energy security. All levels of government can do more to encourage DHS development and bridge the gap toward affecting change.

- Public buildings should lead the way and be the first to connect to DHS
- Main mechanical room located in the basement or ground floor level,
- A centralized water-based (hydronic) heating and cooling system,
- Lowest hot water return temperatures and highest chilled water return temperatures as possible,
- High density or energy usage buildings, situated in close proximity to one another with a variety of usages.

There is often strong resistance to being the first to use a new or different technology or system. By leading the pack, government buildings can reduce the apprehension of other building owners by providing an example to inspire.

- Create a Customer Base

The authors also recommend that municipalities or regional governments establish minimum performance requirements in their jurisdictions.

## 8. FURTHER RESEARCH

To help municipalities and regional governments policy makers must quantify their costs in managing storm water, securing electrical capacity, and addressing energy security in order to realize the potential synergies and cost savings. managersShould design appropriate incentives to reduce overall costs to the municipality.

Electrical utilities are common and the cost of each additional kW of new generation (for each technology) is fairly well studied, however, societal costs are of-ten ignored and focus only on design and construction costs. The cost of overcoming public outrage to this type of infrastructure should be taken into account when determining an overall cost per kW of additional generation. This will help policy makers appreciate the cost of cancelled plants, relocations, and other risks that are often difficult to budget.

## 9. CONCLUSION

It is critical to recognize the benefits of energy reduction techniques and the multiple benefits of DHS to identify eco-efficiency opportunities. municipalities and regional governments can make sustainable initiatives more cost

effective for all parties—and in doing so reduce infrastructure costs and Environmental impact.

Recognizing how systems interact with each other and the benefits they provide is an essential part of developing sustainable systems. The recognition of cost reduction and environmental benefits will allow governments at multiple levels to optimize their municipal service and pollution reduction strategies.

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# Study of Physicochemical Characteristics of the Ganga River

Sakshi Sharma

Subharti Institute of Technology and Engineering, Swami Vivekananda Subharti University, Meerut

**Abstract**—The study was carried out to find the physicochemical characteristics of River Ganga in district Haridwar, Uttarakhand. The surface water samples were collected from four different sites of Haridwar. The objective of the present study is to analyze the physicochemical characteristics of River Ganga in Haridwar at different sites and for the purpose of this study four sites were chosen from Haridwar namely Bhupatwala (Upstream), Harki pauri, Jwalapur and Bahadrad (Downstream). From each site three samples were collected at an interval of 1 week between 10 -11 am. The study focuses on the comparative analysis of physicochemical parameter of river Ganga at four different sites. It is very essential and important to test the water before it is used for drinking, domestic, agricultural or industrial purpose. Water must be tested with different physico-chemical parameters. For the purpose of this study the following parameters were considered namely Temperature, pH, BOD, COD, TDS.

## 1. INTRODUCTION

Water is one of the most important and abundant compounds of the ecosystem. All living organisms on the earth need water for their survival and growth. As of now only earth is the planet having about 70 % of water. But due to increased human population, industrialization, use of fertilizers in the agriculture and man-made activity, the ground water is highly polluted with different harmful contaminants. It is necessary that the quality of drinking water should be checked at regular time interval, because due to use of contaminated drinking water, human population suffers from varied of water borne diseases. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life. It is necessary to know details about different physico-chemical parameters such as color, temperature, acidity, hardness, pH, sulphate, chloride, dissolved oxygen (DO), biochemical oxygen demand (BOD), chemical oxygen demand (COD), alkalinity used for testing of water quality. Heavy metals such as Lead (Pb), Chromium (Cr), Iron (Fe), Mercury (Hg) and etc. are of special concern because they contaminate water and chronic poisoning in aquatic animals. The availability of good quality water is an indispensable feature for preventing diseases and improving quality of life. Rivers are nothing more than surface water flowing down from a higher altitude to a lower altitude due to the pull of gravity. One river might have its source in a glacier, another in

a spring or a lake. Rivers carry dissolved minerals, organic compounds, small grains of sand, gravel, and other material as they flow downstream. Rivers begin as small streams, which grow wider as smaller streams and rivers join them along their course across the land. Eventually they flow into seas or oceans. There has been a steady deterioration in the quality of water of Indian rivers over several decades. India's fourteen major, 55 minor and several hundred small rivers receive millions of liters of sewage, industrial and agricultural wastes. Most of these rivers have been rendered to the level of sewage flowing drains. There are serious water quality problems in the cities, towns and villages using these waters. Water borne diseases are rampant, fisheries are on decline, and even cattle are not spared from the onslaught of pollution. In the Himalayan region the Bhagirathi is joined by the tributaries Alaknanda and Mandakini to form the Ganga. After entering the plains at Haridwar, it winds its way to the Bay of Bengal, covering 2,500 km through the provinces of Uttar Pradesh, Bihar and West Bengal.

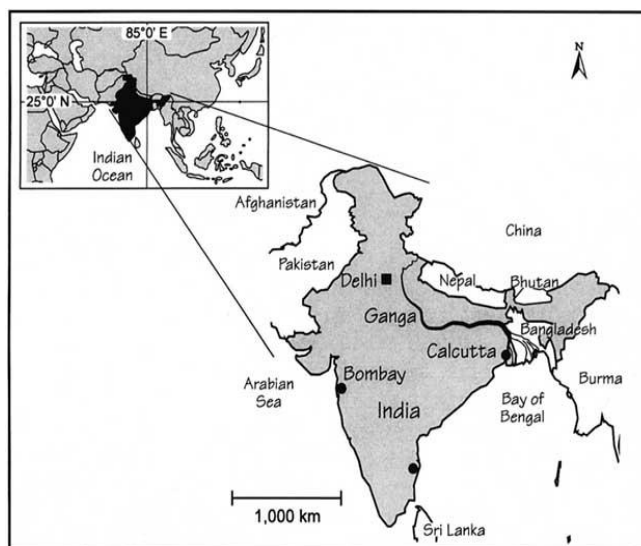


Fig. 1: Reproduced from Water Pollution Control - A Guide to the Use of Water Quality Management Principle Eds by Richard Helmer and Ivanildo Hespahol © 1997 WHO/UNEP ISBN 0 419 22910 8

The present study has been conducted to evaluate the physico-chemical characters of water of river Ganga at four different sites located in city Haridwar (Uttarakhand). These sites were Bhupatwala, Har ki pauri, Jwalapur, Bahadradab. Haridwar is a city in Northern India on the bank of the Ganga River north east of Delhi. It is a Hindu pilgrimage centre. Haridwar lies along the Ganga River at the boundary between the Indo-gangetic plain (South) and the Himalayan foothills (North). The religious importance of Ganga may exceed than that of any other river in the world. From each site three samples were collected at an interval of 1 week between 10 - 11 am.

## 2. MATERIALS AND METHODS

### 2.1 Analytical methods and equipment used in the study

S. no	Parameter	Method	Instrnt/equipment
1	pH	Electrometric	pH Meter
2	TDS	Electrometric	Conductivity/TDS Meter
3	BOD	5 days incubation at 20°C followed by titration	BOD incubator
4	COD	Digestion followed by titration	COD digester

A Total of three surface water samples were taken from each site at an interval of 1 week between 10 am-11am and slightly different results were obtained and an average value of all the parameter is taken. The results obtained from the entire Site are given below in the tabular form.

SITE	TEMPERATURE	pH	BOD (mg/l)	COD (mg/l)	TDS (mg/l)
SITE-I	16.8	7.71	0.1	05	88
SITE-II	17.1	7.70	0.6	08	100
SITE-III	17.2	7.60	0.2	05	50
SITE-IV	17.4	7.60	0.3	07	70

Fig. 2: Average value of physicochemical parameter at all the sites

The average values of the parameters obtained from different sites are given above. At site-I the average value of temperature is 16.8, pH is 7.7, BOD(mg/l) is 0.1, COD(mg/l) is 05, TDS(mg/l) is 88. At site-II the average value of temperature is 17.1, pH is 7.70, BOD(mg/l) is 0.6, COD(mg/l) is 08, TDS(mg/l) is 100. At site -III the average value of temperature is 17.2, pH is 7.60, BOD (mg/l) is 0.2, COD (mg/l) is 05, and TDS (mg/l) is 50. At site-IV the average value of temperature is 17.4, pH is 7.60, BOD (mg/l) is 0.3, COD (mg/l) is 07, and TDS (mg/l) is 70.

According to the standards given by BIS(Bureau of Indian standards) for drinking water the value of the pH lies between 6.5-8.5. The value of permissible limit of BOD lies

up to 5mg/l. The value of COD is up to 10mg/l. The value of the permissible limit for TDS lies between 200-500. There is not as such limit prescribed for Temperature but according to BIS temperature of river water up to 40°C is suitable for drinking.

### 3. PERMISSIBLE LIMITS OF THE PHYSICO-CHEMICAL PARAMETERS BY BIS

S. NO	Parameter	Permissible limit for drinking water
1	pH	6.5-8.5
2	BOD	5
3	COD	10
4	TDS	200-500
5	Temperature	<40°C

### 4. RESULT & DISCUSSION

The results obtained from analysis of water samples of river Ganga are shown in above tables.

The reported values refer to the mean value of water samples collected from different sites along the stretch of Ganga River. The results indicate that the quality of water varies inconsiderably from location to location. A summary of the findings is given below:

In the present study the water temperature range of River Ganga in Haridwar was recorded between 16.8-17.4. WHO (1993) did not recommend any definite temperature value for drinking water. A temperature of about 40°C is permissible limit for drinking water (BIS 1991). Temperature below 14°C and above 39.5°C is harmful for fish (Hossain *et al.*, 2008) [10]. Hence it can be concluded that the water temperature of River Ganga in Haridwar is suitable for both drinking purpose and fish production.

In the current study the pH was found ranging between 7.1 - 7.6. pH as such has no adverse effect on health, however a lower value below 4 will produce sour taste and a higher value above 8.5 an alkaline taste. pH range from 6.5 to 7.5 is most favorable for production in a water body. The WHO and BIS recommendation of pH is 6.5- 8.5. In the current study the pH range is a safe for aquatic life and drinking water.

In the present study BOD varies from 0.1-0.6 mg/l. The BIS (1991) has set desirable limit of BOD value to be 05 mg/l. In the present Study BOD values were found well within the standard permissible limit which accounts for its suitability for use.

In the present study COD varies from 05-08 mg/l. The BIS (1991) has set desirable limit of BOD value to be 10mg/l. In the present Study BOD values were found well within the standard permissible limit which accounts for its suitability for use.

In the present study TDS varied from 50 mg/l - 100 mg/l. The BIS (1991) has set desirable limit of TDS value to be 500 mg/l

in potable water. However the permissible limit is 2000 mg/l in the absence of any alternative source in water. According to WHO (1993), the standard permissible limit for TDS is 1000 mg/l. Water at a TDS level of above 500 mg/l is unsuitable for flora and tastes unpleasant to drink. In the present study TDS values were found well within the standard permissible limit which accounts for its palatability

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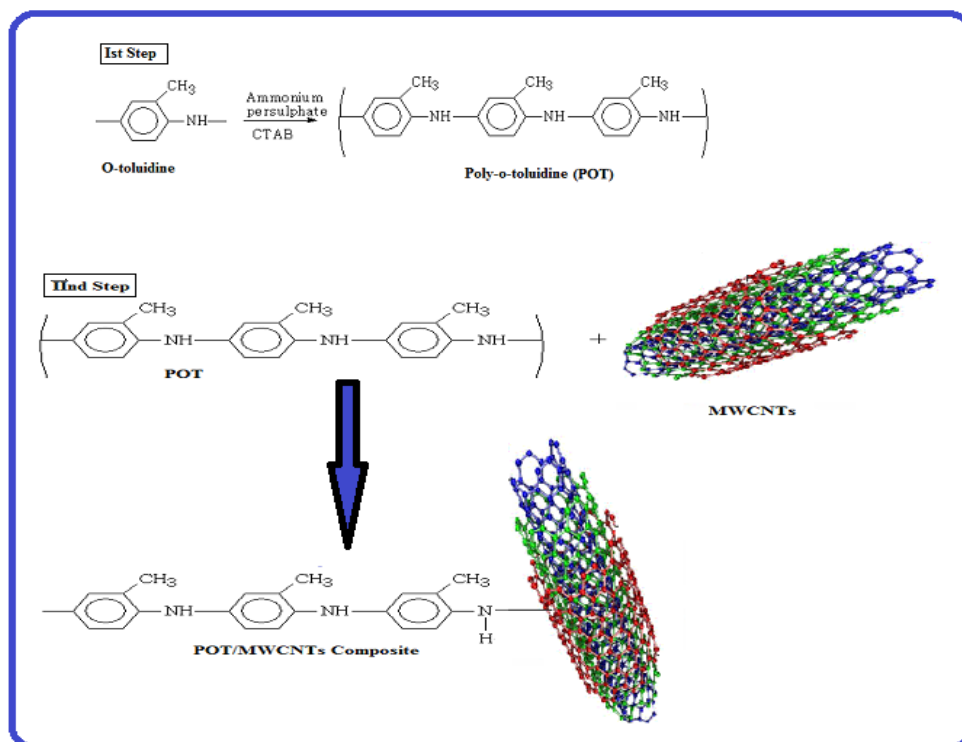
# Electrically Conducting and Isothermal Stability Studies of Facile Synthesized Poly-*O*-Toluidine/Multi-Walled Carbon Nanotubes Composite

Shakeeba Shaheen

Analytical and Polymer Research Laboratory, Department of Applied Chemistry,  
F/O Engineering and Technology, Aligarh Muslim University Aligarh 202002, India  
E-mail: shakeebashaheen@ymail.com

**Abstract**—Poly-*o*-toluidine (POT) based composite was prepared with multi-walled carbon nanotubes (MWCNTs) by *in-situ* oxidative polymerization. POT and POT/MWCNTs composites were characterized by Fourier transform infra-red spectroscopy (FTIR), X-ray diffraction (XRD), Scanning electron microscopy (SEM), Transmission electron microscopy (TEM), UV-visible spectra and thermogravimetric analysis (TGA). The TGA studies revealed that POT/MWCNTs composite was thermally more stable in comparison to pure polymer. The electrical conducting behavior of POT/MWCNTs was observed better than pure POT. The stability of POT and POT/MWCNTs composites in terms of DC electrical conductivity retention was found to be fairly good as studied by isothermal technique. The POT and POT/MWCNTs composites can be used in electrical and electronic applications below 90 °C under ambient conditions

**Keywords:** MWCNTs; Poly-*o*-toluidine; Electrical conductivity; Thermal stability; Isothermal Stability.



# Influence of Modifier Oxide on the thermoluminescence and Dosimetric Characteristics of Lithium Borate Glasses Doped with $\text{Pr}^{3+}$ ions

J. Anjaiah<sup>1</sup> and C. Laxmikanth<sup>2</sup>

<sup>1</sup>Department of Physics, Geethanjali College of Engg & Technology, Keesara, RR Dist., 501 301, India

<sup>1</sup>Department of Physics, The University of Dodoma, Tanzania

<sup>2</sup>Department of Physics, The University of Dodoma, Tanzania

E-mail: <sup>1</sup>[anjaiah.juluru@gmail.com](mailto:anjaiah.juluru@gmail.com), <sup>2</sup>[htnakimxal@gmail.com](mailto:htnakimxal@gmail.com)

**Abstract**—Thermoluminescence (TL) characteristics of X-ray irradiated pure and doped with  $\text{Pr}^{3+}$  ions  $\text{Li}_2\text{O-MO-B}_2\text{O}_3$  (where  $\text{MO}=\text{ZnO}, \text{CaO}, \text{CdO}$ ) glasses have been studied in the temperature range 303-573K; all the pure glasses have exhibited single TL peak at 382K, 424K and 466 K respectively. When these glasses are doped with  $\text{Pr}^{3+}$  ions no additional peaks are observed but the glow peak temperature of the existing glow peak shifted gradually towards higher temperatures with gain in intensity of TL light output. The area under the glow curve is found to be maximum for  $\text{Pr}^{3+}$  doped glasses mixed with cadmium oxide as modifier. The trap depth parameters associated with the observed TL peaks have been evaluated using Chen's formulae. The possible use of these glasses in radiation dosimetry has been described. The result clearly showed that praseodymium doped cadmium borate glass has a potential to be considered as the thermoluminescence dosimeter.

## 1. INTRODUCTION

Thermoluminescence is the phenomenon of emission of light from a solid which has been previously exposed to ionizing radiation under conditions of increasing temperature. Oxyliumborate glasses are considered as good materials for dosimetry applications since they are relatively moisture resistant when compared with the pure borate glasses. The understanding of the glass structure by detailed studies on radiation induced defect centres has been an interesting subject of investigation in recent years. Recently some recommendable work has done on thermoluminescence mechanisms in borate based glasses. Rojas et al. reported the structural, thermal and optical properties of  $\text{CaBO}$  and  $\text{CaLiBO}$  glasses doped with  $\text{Eu}^{3+}$  [1]. Thermoluminescence study of  $\text{MnO}$  doped borophosphate glass samples for radiation dosimetry is reported by B.J.R.S. Swamy et al. [2] and the thermoluminescence response of copper-doped potassium borate glass subjected to 6 megavolt x-ray irradiation is reported by I. Hossain et al. [3]. Thermoluminescence properties of  $\text{CaO-B}_2\text{O}_3$  glass system doped with  $\text{GeO}_2$  reported by T.N.H. Tengku Kamarul Bahri et al. [4]. Haydar Aboud et al. reported the

thermoluminescence properties of the Cu-doped lithium potassium borate glass [5].

It is well known that boric acid ( $\text{B}_2\text{O}_3$ ) is one of the good glass formers and can form glass alone with good transparency, high chemical durability, thermal stability and good rare-earth ion solubility [6]. The glass containing  $\text{Li}_2\text{O}$  as network modifier was seen as bubble free, highly stable and moisture resistant, suitable for a systematic analysis [7]. Among the three modifier oxides chosen to mix in the present glass system, viz.,  $\text{CaO}$ ,  $\text{ZnO}$  and  $\text{CdO}$ ;  $\text{ZnO}$  is expected to shorten the time taken for solidification of glasses during the quenching process and glasses containing  $\text{ZnO}$  have high chemical stability and less thermal expansion. Their wide band gap, large exciton binding energy and intrinsic emitting property make them as promising candidates for the development of optoelectronic devices, solar energy concentrators, ultraviolet emitting lasers and gas sensors [8]. Both  $\text{ZnO}$  and  $\text{CdO}$  are thermally stable and appreciably covalent in character [9].

Lithium tetraborate glass system is a known and important starting material in the development of applications of radiation dosimetry for a long period, since its effective atomic number  $Z_{\text{eff}} \approx 7.25$  has the property of being nearly tissue equivalent that makes it as a very promising material in the field of personal and clinical dosimetry and for other applications like X-ray phosphors, scintillators and thermoluminescent detectors [2,10-13]. However, pure borate glasses have certain disadvantages to use in radiation dosimetry since they are highly hygroscopic and exhibit weak glow peak at relatively low temperatures.

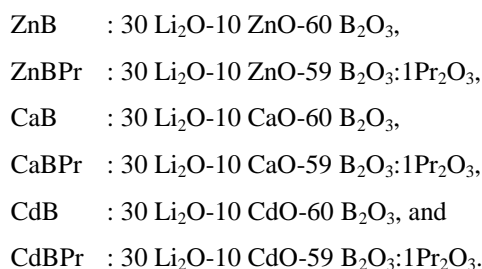
Schulman et al. [14] were the first to be acknowledged for starting the TL studies on lithium borate compounds and since then various details on TL studies of alkali and alkaline earth tetra borates continued up to present times especially on magnesium and lithium borate compounds. Several attempts were also made to enhance thermoluminescence (TL)

sensitivity of these glass materials by adding different transition and rare earth or lanthanide metal ions to these glass samples [15-20].

The study on the influence of praseodymium ions on thermoluminescence light output of these glasses is also carried out with a view to examine the suitability of these glasses in the radiation dosimetry.

## 2. EXPERIMENTAL METHODS

Undoped and following praseodymium ion doped glasses in mole% are prepared by using standard melting and quenching techniques and used for the present study. [21-23].



Appropriate amounts of raw materials ZnO, CaCO<sub>3</sub>, CdO, H<sub>3</sub>BO<sub>3</sub>, Li<sub>2</sub>CO<sub>3</sub> and Pr<sub>2</sub>O<sub>3</sub> were thoroughly mixed and grounded in an agate mortar and melted in a platinum crucible. The chemicals used in the work were of high purity (99.9%). These compositions were heated in a PID temperature controlled furnace at 450°C for 2 hour for the decarbonization from CaCO<sub>3</sub> and Li<sub>2</sub>CO<sub>3</sub> and then the temperature maintained within the range 1000-1050°C and kept the melt at this temperature for an hour till a bubble free liquid was formed. The crucibles were shaken frequently for the homogeneous mixing of all the constituents. The resultant melt was poured on a rectangular brass mould held at room temperature. The samples were subsequently annealed at glass transition temperature in another furnace to remove mechanical stress and were polished.

The density 'ρ' of these glasses was determined by the standard principle of Archimedes' using xylene (99.99% pure) as the buoyant liquid. The glass transition temperatures  $T_g$  and crystallization temperature  $T_c$  of these glasses were determined (to an accuracy of  $\pm 1$  °C) by differential scanning calorimetry (DSC) traces, recorded using universal V23C TA differential scanning calorimeter with a programmed heating rate of 15 °C per minute in the temperature range 30-750 °C.

Infrared transmission [IR] spectra for these glasses were recorded using a Perkin Elmer Spectrometer in the wavenumber range 400-4000 cm<sup>-1</sup> by KBr pellet method. For recording thermoluminescence emission, the glasses were irradiated with X-rays for one hour with Norelco X-ray Unit operated at 35 kV, 10 mA; thermoluminescence output of these glasses was recorded on a computerized Nucleonix-TL set up with a heating rate of 1 °C/s.

## 3. RESULTS AND DISCUSSION

### 3.1 Physical properties and characterization

From the measured values of density and the average molecular weight  $\bar{M}$ , various other physical parameters such as praseodymium ion concentration  $N_i$ , mean praseodymium ion separation distance and field strength are calculated and presented in the Table 1.

**Table 1: Various physical properties of Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub>: Pr<sub>2</sub>O<sub>3</sub> glasses**

Property/ Glass	ZnB	ZnB Pr	CaB	CaB Pr	CdB	CdB Pr
Refractive index, $n_d$	1.51 7	1.528	1.51 9	1.530	1.52 3	1.538
Density, $\rho$ (g/cm <sup>3</sup> )	2.18 1	3.06 7	2.41 5	3.192	2.79 9	3.443
Average molecular weight, $\bar{M}$	46.0 01	44.81 8	46.0 17	44.82 0	46.0 28	44.83 1
Pr <sup>3+</sup> ion concentration, $N_i$ (10 <sup>22</sup> /cm <sup>3</sup> )	--	4.122	--	4.290	--	4.63
Inter-ionic distance of Pr <sup>3+</sup> ions, $R_i$ (Å)	--	2.895	--	2.857	--	2.79

Our visual examination, absence of peaks in X-ray diffraction spectra, existence of glass transition temperature  $T_g$  and crystallization temperature  $T_c$  in differential thermal analysis curves, indicate that the glasses prepared were of amorphous in nature.

Fig.1 represents the thermograms of pure and Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub>:Pr<sub>2</sub>O<sub>3</sub> glasses; the pure glasses exhibit an endothermic effect due to the glass transition temperature  $T_g$ . Presence of single transition temperature  $T_g$  at 553°C in ZnB glass, 544.7°C in CaB glass and 537°C in CdB glass indicates homogeneity of the glasses. At still higher temperatures an exothermic peak  $T_c$  due to the crystal growth followed by an endothermic effect due to the re-melting of the glass symbolized by  $T_m$  are observed. The glass forming ability (Hruby's) parameter  $K_{gl} = (T_c - T_g)/(T_m - T_c)$  is calculated, which gives the information about the stability of the glass against devitrification [24,25] are evaluated and presented in Table 2.

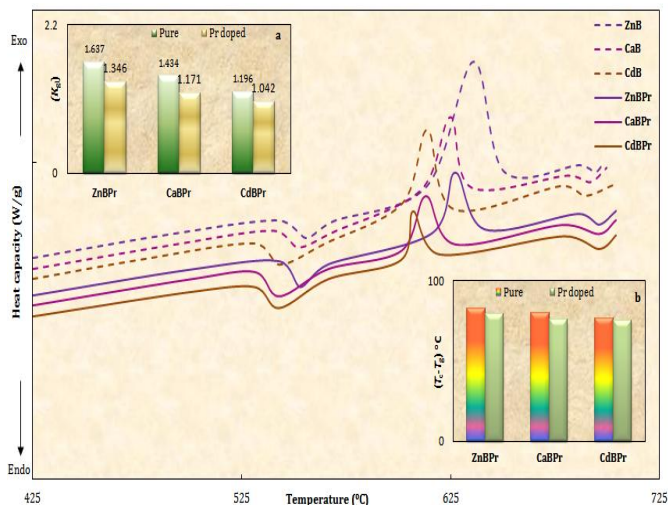
**Table 2: Data on differential scanning calorimetric studies of Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub>: Pr<sub>2</sub>O<sub>3</sub> glasses.**

Glass	$T_g$ (°C)	$T_c$ (°C)	$T_m$ (°C)	$T_g/T_m$	$(T_c - T_g)$ (°C)	$(T_c - T_g)/T_m$	$K_{gl}$
ZnB	553.0	636	686.7	0.805	83.0	0.121	1.63 7
ZnBP r	547.6	627	686.0	0.798	79.4	0.116	1.34 6
CaB	544.7	625	681	0.800	80.3	0.118	1.43 4
CaBP r	536.9	613	678	0.792	76.1	0.112	1.17 1



CdB	537.0	613.8	678	0.792	76.8	0.113	1.196
CdBPr	532.0	607	679	0.784	75.0	0.110	1.042

The highest values of these parameters are obtained for ZnO-modifier glass (ZnBPr) indicating its relatively high glass forming ability among the three glasses. Insets of Fig.1 represent; (a) the variation of Hrubby's parameter and (b) the variation of (T<sub>c</sub>-T<sub>g</sub>) for pr<sup>3+</sup> ions doped glasses mixed with different modifier oxides.



**Fig. 1:** DSC patterns of pure and Pr<sup>3+</sup> doped Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> glasses. Insets a) the variation of Hrubby's parameter and b) the variation of (T<sub>c</sub>-T<sub>g</sub>) for different modifier oxides.

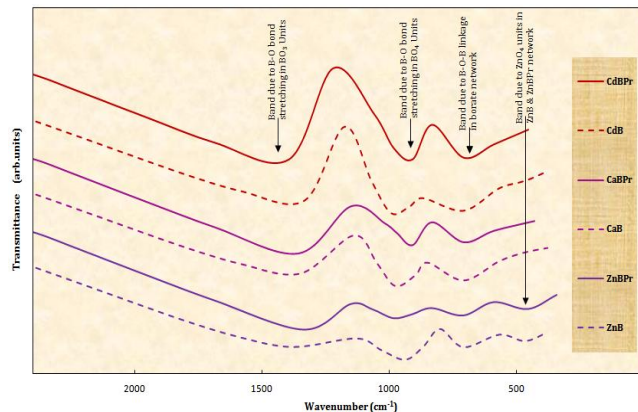
For the pr<sup>3+</sup> ions doped glasses mixed with different modifier oxides, the glass transition temperature T<sub>g</sub> is in between 532 °C and 547.6 °C. For all glasses with the introduction of praseodymium ions the values of T<sub>g</sub> and T<sub>c</sub>-T<sub>g</sub> is found to decrease gradually.

### 3.2 Infrared Spectroscopy

Fig. 2 represents IR spectra of the pure as well pr<sup>3+</sup> ions doped Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> glasses. The infrared transmission spectra of pure and praseodymium ion doped Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> glasses exhibit three groups of bands: (i) in the region 1320-1380 cm<sup>-1</sup>, (ii) in the region 930-1010 cm<sup>-1</sup> and (iii) a band at about 710 cm<sup>-1</sup>.

It is well known that the effect of introduction of alkali oxides into B<sub>2</sub>O<sub>3</sub> glass is the conversion of sp<sup>2</sup> planar BO<sub>3</sub> units into more stable sp<sup>3</sup> tetrahedral BO<sub>4</sub> units and may also create non-bridging oxygens. Each BO<sub>4</sub> unit is linked to two such other units and one oxygen from each unit with a praseodymium ion and the structure leads to the formation of long tetrahedron chains. The presence of such BO<sub>4</sub> units in the present glasses is evident from the IR spectral studies. The second group of bands is attributed to such BO<sub>4</sub> units where as the first group

of bands is identified as due to the stretching relaxation of the B-O bond of the trigonal BO<sub>3</sub> units and the band at 710 cm<sup>-1</sup> is due to the bending vibrations of B-O-B linkages in the borate network [26-29]. A weak band observed around 456 cm<sup>-1</sup> is an indicative of the presence of ZnO<sub>4</sub> units in the ZnB series glass network [30,31].



**Fig. 2:** Infrared spectra of pure (dotted line) and Pr<sup>3+</sup> doped (solid line) Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> glasses.

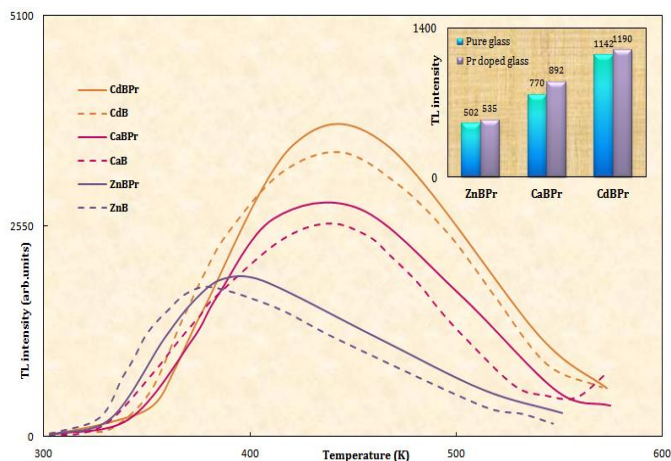
The intensity of the second group of bands (band due to the trigonal BO<sub>4</sub> units) is found to increase at the expense of first group of bands (bands due to tetrahedral BO<sub>3</sub> units) with the introduction of Pr<sup>3+</sup> ions with the shifting of meta-centres of first and second group of bands, respectively towards slightly lower and higher wave number for all the glasses. No significant change in position and intensity of the other bands are observed in the spectra of the glass by introducing the praseodymium ions. The summary of the data on the positions of various bands in the IR spectra of pure and Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub>:Pr<sub>2</sub>O<sub>3</sub> glasses are presented in Table 3.

Glass	Band due to B-O bond stretching in BO <sub>3</sub> units	Band due to B-O bond stretching in BO <sub>4</sub> units	Band due to B-O-B linkage in borate network
ZnB	1378	939	710
ZnBPr	1367	954	710
CaB	1352	979	710
CaBPr	1343	989	710
CdB	1336	992	710
CdBPr	1329	1008	710

### 3.3 Thermoluminescence

Thermoluminescence glow curves of all the glasses doped with praseodymium ions have shown in Fig 3. Pure Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> (M=ZnO, CaO and CdO) glasses exhibit a glow peak at 382K in ZnB glass, 424K in CaB glass and 466 K in CdB glass. When these glasses are doped with Pr<sup>3+</sup> ions no additional peaks are observed but the glow peak temperature

$T_m$  of the existing glow peak shifted gradually towards higher temperatures with a gain in the intensity of TL light output. The glow peaks of praseodymium ion doped ZnBPr, CaBPr and CdBPr glasses shifted to 386K, 432K and 469K respectively.



**Fig. 3: Thermoluminescence emission of pure (dotted line) and  $\text{Pr}^{3+}$  ions doped (solid line)  $\text{Li}_2\text{O-MO-B}_2\text{O}_3$  glasses. Inset figure represents the relative TL light output of pure and  $\text{Pr}^{3+}$  ions doped glasses**

The relative TL light outputs (area under the glow curve) of pure and  $\text{Pr}^{3+}$  ion doped  $\text{Li}_2\text{O-MO-B}_2\text{O}_3$  glasses have shown in the inset of Fig. 3. Pure glasses have the TL light output intensity area under the glow curve is 502, 770 and 1142. The area under the glow curve is also found to be maximum for CdBPr doped glass comparing to all other glass systems.

The trap depth parameters for these glow peaks are computed using Chen's formulae.

The activation energies for these glow peaks are computed using Chen's formulae [32]:

$$E_\tau = 1.52 (k_B T_M^2 / \tau) - 1.58 (2k_B T_M),$$

$$E_\delta = 0.976 (k_B T_M^2 / \delta), \text{ for the first order kinetics.}$$

In the above equation  $k_B$  is Boltzmann constant,  $\tau = T_M - T_1$ ,  $\delta = T_2 - T_M$ ,  $\mu_g = \delta / (T_2 - T_1)$ , where  $T_M$  is the glow peak temperature and  $T_1$  (rising end) and  $T_2$  (falling end) are the temperature at the half widths of the glow peaks. The summary of the data on thermoluminescence peaks with corresponding trap depth parameters of the present glasses is furnished in Table 4. The trap depth parameters of pure glasses are found to be  $\sim 0.422$  eV and observed to increase by doping with  $\text{Pr}_2\text{O}_3$ . Such value of trap depth indicates that the lifetime ( $\tau$ ) of electron in these traps is of the order of several months [2, 33].

Prior to TL measurements, the optical absorption spectra of all the glasses before and after X-ray irradiation are recorded. After the X-ray irradiation no additional absorption bands are observed other than those obtained in non-irradiated glasses;

however the relative intensities of these bands are slightly affected [34].

**Table 4: Data on various trap depth parameters of  $\text{Li}_2\text{O-MO-B}_2\text{O}_3: \text{Pr}_2\text{O}_3$  glasses**

Glass	TM (K)	$\tau$ (K)	$\delta$ (K)	$\mu_g$	$E_\tau$ (eV)	$E_\delta$ (eV)	TL light output (rel. units)
ZnB	382	30	28	0.483	0.526	0.432	502
ZnBPr	386	29	27	0.482	0.560	0.458	535
CaB	424	53	35	0.398	0.324	0.426	770
CaBPr	432	54	34	0.386	0.330	0.455	892
CdB	466	76	44	0.367	0.244	0.409	1142
CdBPr	469	74	43	0.368	0.258	0.424	1190

The action of X-ray irradiation on glasses is to produce secondary electrons from the sites where they are in a stable state and have an excess energy. Such electrons may traverse in the glass network depending upon their energy and the composition of the glass and are finally be trapped, thus forming color centres (or alternatively they may form excitons with energy states in the forbidden gap). The trapping sites may be the praseodymium ions which constitute the glass structure, ions of admixtures to the main composition and the structural defects due to impurities in the glass. Thus this process leads to the formation of 1) boron electron centres, 2) non-bridging oxygen hole centres and 3) boron oxygen hole centres [35-37]. Thermoluminescence is a consequence of radiative recombination between the electrons (released by heating from electron centre) and an anti bonding molecular orbital of the nearest of the oxygen hole centres. The observed TL peaks in the present glasses can be attributed due to such radiation.

The  $\text{Li}^+$  ions have closed structure, do not have energy levels within 10 eV of the ground state and hence these ions do not participate directly in luminescence but may act as activator ions [38]. Let us assume that the  $\text{Pr}^{3+}$  ions are uniformly distributed throughout the sample. In the absence of  $\text{Pr}^{3+}$  ion in the network, each electron released by heating from electron centre would be caught by an anti-bonding molecular orbital of the nearest of the oxygen hole centre. The process is followed by a radiative recombination. The observed TL peak in the present glasses is attributed to such radiation. If  $\text{Pr}^{3+}$  ion is present in the glass network, we have observed such a radiative recombination to enhance with respect to that of corresponding pure glass indicating that the praseodymium ions are acting as TL activators in all the glasses. The comparison of TL emission of  $\text{Pr}^{3+}$  doped glasses shows a low percentage of enhancements of TL light output for ZnBPr glasses.

The larger the number of  $\text{Pr}^{3+}$  ions in the glass network, the higher is the TL light output. Relatively larger concentration  $\text{Pr}^{3+}$  ions in CdBPr glasses cause relatively higher light output as observed (Inset of Fig. 3). Thus the analysis of the TL data

of Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub>:Pr<sub>2</sub>O<sub>3</sub> glasses suggests that the CdBPr glass to be a better candidate for thermoluminescence emission among the three Pr<sup>3+</sup> doped glasses.

#### 4. CONCLUSIONS

Finally our studies on properties of Li<sub>2</sub>O-MO-B<sub>2</sub>O<sub>3</sub> glasses doped praseodymium ions indicate that i) Differential scanning calorimetric studies indicate high glass forming ability is for ZnBPr glass. ii) The IR spectral studies indicate relatively less disorder in ZnBPr glass network. iii) The analysis of the TL data suggests that the CdBPr glass can be used more effectively in radiation dosimetry since they exhibit high TL light output in high temperature region.

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# A Study on Feasibility of Cold Storage and Food Processing Units for Pineapple in Assam

Vivek Kr. Pathak<sup>1</sup>, HIRAK Chakraborty<sup>2</sup> and K.M Pandey<sup>3</sup>

<sup>1</sup>Department of Humanities & Social Sciences NIT Silchar

<sup>2</sup>Department of management Studies NIT Silchar

<sup>3</sup>Department of Mechanical Engineering NIT Silchar

E-mail: <sup>1</sup>[iampathak.v@gmail.com](mailto:iampathak.v@gmail.com), <sup>2</sup>[hirak\\_raj@rediffmail.com](mailto:hirak_raj@rediffmail.com), <sup>3</sup>[kmpandey2001@yahoo.com](mailto:kmpandey2001@yahoo.com)

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**Abstract**—North-Eastern region of India is endowed with varieties of fruits, vegetables and other agro-products and has the potential to be a sunrise zone for food processing and other agri-product based businesses. This paper deals with immense opportunities present in food processing in the region. It is observed that simple value addition like cleaning, sorting and packaging can increase the quality and durability of the produce as well as it helps in improving the economic condition of the farmers also in return. It is also observed in the study that this sector is not delivering the desired output because it is still highly unorganized, inefficient, and unprofitable in spite of having various policies and schemes for the development of this sector by various governmental agencies. It is also established in the study that the development of food processing sector in North East Region of India is mired due to poor infrastructure, poor connectivity with potential markets, inadequate and inefficient supply chain, insufficient power supply and pitiable irrigation facilities. Many growers and farmers are shifting from pineapple to rubber plantation due to acute lack of cold storages and food processing units in the region. A purposive sampling has been used for selecting the farmers/owners of the pineapple plantation. The study also targets the sellers and the consumers of Pineapple. Questionnaire was prepared for collecting the primary data and various reports from the government agencies were used for secondary data for analysis in the study.

## 1. INTRODUCTION

India is a richly endowed agricultural nation. India has all major climates of the world, enjoys long sunshine hours, fairly good rainfall which are ideally suited for round the year cultivation. It has the largest cattle population, second largest goat and sheep population and a vast coastline. Given the resource endowment, India has all the potential to become one of the largest food processing nations in the world. Potential for production is also matched by strong demand for processed food products due to rapid urbanization, change in preferences and practices in consumption.

Horticulture crops form a significant part of the total agriculture produce in the country comprising of fruits, vegetables, root and tuber crops, flowers, medicinal and aromatic plants, spices and condiments etc.

Horticultural development in the country continues to make steady progress in terms of production and exports. Past years have seen a significant increase in the area, productions and productivity in horticultural crops in the country.

In an emerging country like India, where growth with equity is a primary policy thrust, the optimum development of the food processing sector will contribute significantly in tackling several developmental concerns such as disguised unemployment in agriculture, rural poverty, food security, food inflation, improved nutrition, prevention of wastage of food, etc. By serving as a bridge between agriculture and manufacturing and by dealing with a basic need of all Indian citizens the assured supply of healthy and affordable food at all locations in the country, this sector has the potential to be a major driver in India's growth in coming years.

India's appalling state of food wastage is docketed to the insufficient cold chain facilities in the nation. India is among the top producers of fruits & vegetables and also faces the highest amount of wastage in the category. Inappropriate food/cold storage facilities not only affect the quality and freshness of the food but also severely affect the food prices in the nation.

All the eight North Eastern states produce pineapple. The advantageous position of North Eastern Region in terms of fertile and organically rich soils, abundant rainfall, water resources and great agro-climatic diversity supports the cultivation of best quality pineapple in the region. The region produces more than 40% of pineapple produced in the country and almost 90%-95% of the produce is organic. Pineapple produced in the region is qualitatively different and is said to be among the best in the world as they are sweet with less fibre.

Pineapple is a perennial crop with an economic life of 5-7 years, however, in the North Eastern region; the farmers cultivate it beyond 12-15 years through crop manipulation and traditional agronomic practices. In many parts of North Tripura and in the Barak Valley of Assam, even 20-25 year

old plantations can be seen. In the region, Assam, Tripura, Meghalaya and Nagaland are major pineapple producing states.

There are two popular varieties of pineapple cultivated in North East popularly known as:

- a. Kew (also known as Smooth Cayenne) – Suitable for canning with an average fruit weight of 2-3 kg.
- b. Queen – Table fruit variety with an average fruit weight of 1-2 kg.

Assam is the largest producer of fruits and vegetables in the northeast region and contributes 60% to the total horticulture production of the region. It acts as a gateway for marketing of horticulture produce from northeast to rest of the country.

Horticultural crops in the state occupy nearly 15% of the gross cultivated area and the state produces more than 15.0 lakh MT of fruits, 29.0 lakh MT of vegetables and 1.0 lakh MT of spices besides nut crops, flowers and medicinal & aromatic plants annually. In spite of having such inherent potential, commercialization of horticulture sector in Assam has not yet happened. From the productivity point of view, productivity of fruits in the state is more (13.50 MT/ha) as compared to national level (11.73 MT/ha) and NE Region (8.57 MT/ha). Productivity of vegetables in the state is found to be less (11.25 MT/ha) in comparison to national level (17.25 MT/ha) but more than NE Region (10.13 MT/ha). This situation leads to the opportunity of productivity enhancement.

In Assam, pineapple is cultivated in all districts, while the identified clusters for pineapple cultivation are Cachar, Kamrup, Sonitpur, Karbi Anglong and Dima Hasao. Kew, Giant Kew and Queen are the major varieties grown in the state.

## 2. PROBLEM STATEMENT

The North East Region of India alone produces more than 40% of the total pineapple of the country and 90 to 95% of the produce is organic. Pineapples produced from this region are qualitatively different and are said to be among the best in the world. The state of Assam ranks second among all the states of India in terms of pineapple production. Despite having good production figures the region underperforms in terms of productivity and marketing the product. During the peak season, the markets are covered with big heaps of pineapple, which leads to a glut in the market. Of the total production, barely any of the fruit is processed, the rest being consumed in the fresh form, which leads to a very low price. There is no regular market in most of the production zones and a large quantity of pineapple gets wasted in the field itself. No value addition is being undertaken by the farmers at the field level. The fruit being perishable has a short shelf life. The absence of any kind of cold chain adds to the post-harvest wastages. Before going for any recommendation for setting up of cold

storage facility and/or food processing units, this feasibility study becomes very crucial.

### 2.1 Objective of the Study

1. To recognize the pineapple production in the study area and find out the prospects of further growth prospects..
2. To study and analyze the feasibility of cold storages and processing units for pineapple in the region.

## 3. RESEARCH METHODOLOGY

### Data Source

*Primary Data:* Primary data source are the pineapple cultivators, sellers and the intermediaries.

*Secondary Data:* For secondary data, sources such as vision documents of North Eastern Region, Government of India publications, Reports of National Horticulture Board, Indian Institute of Horticulture Research, Ministry of Food Processing Industries, etc. were used.

### Data Collection Methods

For Primary data collection a schedule was prepared and information from designated officials, cultivators, sellers and intermediaries was collected through personal interactions.

The secondary data were available in a readymade format over the internet and in the offices. Exhaustive desk research was undertaken based on published information such as state profiles, research reports, publications of government officials and other sources.

### Sampling Technique:

*Sample Size-* 18 farmers were selected who were the owner of the plantations. They also employed other farmers under them who were basically not the owner of any plantation or owned a small plantation.

*Sampling Type-* Purposive Sampling.

*Target-* Pineapple Growers/farmers, sellers and consumer.

### Limitations of the Study

Due to constraints of time and resources the study is likely to suffer from certain limitations. Some of them are

- a. The information given by the respondents might be biased because some of them might not be interested in providing correct information.
- b. The officials supported a lot but did not have sufficient time to clear all the points.
- c. Since majority of the farmers are shifting from pineapple production to rubber plantation so the collection of the pineapple production data faced hurdles regarding the land engaged by the farmers in pineapple production.
- d. Various data were given just verbally by the officials.
- e. Some of the data available may not be updated.



#### 4. LITERATURE REVIEW

In the paper, Food Processing Industry: Opportunities in North East Region of India, Mohammad Rais, Shatroopa Acharya and Gary W. Vanloon has observed that The food processing industry has made some significant progress in the North Eastern Region. Through arrival of MNC's and locals realizing the potential, the sector is all set to boom. Yet, the sector continues to face many challenges. Originating within a difficult geo-physical terrain, varied socio-economic conditions, poor road connectivity and environment problems, the sector is cluttered with complications. The geo-physical terrain of the region with widely scattered diverse tribal communities is itself a huge challenge in formation of a cohesive socio-economic policy for the region. Hence, there is a need of special approaches to deal such issues <sup>[1]</sup>.

In a research report, titled Export Potential of Horticultural Products from North Eastern States published by APEDA, it is mentioned that in the year 2004-2005 there was a surplus production of 1,84,319 metric tonnes of pineapple <sup>[2]</sup>.

**Table 1: Surplus Quantities Of Major Horticulture Products In North Eastern States.**

Commodity	Citrus	Banana	Pineapple	Papaya	Jackfruit	Ginger	Turmeric	Potato	Chillies
Arunachal Pradesh	18702	10168	24919	-	-	25163	-	-	-
Assam	12000	85000	29000	15000	25000	42000	-	-	-
Manipur	1962	-	24000	5320	-	7045	-	-	22200
Meghalaya	23000	-	70000	-	-	35048	6900	117500	-
Mizoram	5300	1200	-	-	-	16500	400	-	424
Nagaland	2000	-	5400	-	-	-	-	1750	-
Sikkim	1100	-	-	-	-	24300	1300	32612	-
Tripura	10500	-	31000	-	93000	960	1600	-	11650
<b>Total</b>	<b>74564</b>	<b>96368</b>	<b>184319</b>	<b>20320</b>	<b>118000</b>	<b>151016</b>	<b>10200</b>	<b>151862</b>	<b>34274</b>

In the paper, Financial Viability, Value Addition and Constraint Analyses of Certified Organic Pineapple Production and Marketing in Ghana, John K.M. Kuwornu, Abdulai A. Nafeo and Yaw B. Osei-Asare have assessed the value added by the farmer, retailer and processor. It established that the processor adds the highest value per metric tonne of pineapple fruits followed by fresh fruit retailer and then the farmer. On the average the pineapple drying processor adds the highest total value per tonne of fresh pineapple followed by the slicing processor and then juicing processor. On the whole, the drying processor incurs the highest cost per tonne and hence sells at a higher price to obtain a value to recover cost and make some profit to remain in business compared to the slicing and then juicing processor. On a daily basis, the drying processor adds the highest value

followed by the slicing processor, the juicing processor, the retailer and then the farmer <sup>[3]</sup>.

From the Economic Survey of Assam conducted in the year 2012-2013, it can be inferred that as per the data available from Agriculture Department, Assam has brought tremendous change in the production of fruits, spices and vegetables and thereby opening ample scope for setting up of food processing industries in the state.

At present less than 30% of the food products are processed in the state, of which 80% of the processing industry is concentrated upon rice, tea, milk, flour, spices, etc. Processing and packaging of perishable fruits and vegetables does not have desired importance due to non-availability of sufficient storage units <sup>[4]</sup>.

In a report published by ONICRA on Food Processing Industry in India, the agency identified Food Processing Industry (FPI) in India as a sunrise sector that has gained prominence in the recent years. Easy availability of raw materials, changing lifestyles and favourable fiscal policies has given a considerable push to the industry's growth <sup>[5]</sup>.

The Department of Horticulture, Government of Assam, had published "Horti Vision 2020" in which the department has identified Assam as a 'Sleeping Giant' for the wide range of horticultural crops. Identifying the scope of growth in the sector, it had listed a number of steps for increase in production and quality <sup>[6]</sup>.

In the report titled India's North-East - Diversifying Growth Opportunities, the Indian Chamber of Commerce has identified that to be socially, and economically sustainable, India's growth story needs to be inclusive. However, the country's north east has been experiencing a comparatively slower pace of industrialisation and socio-economic growth. Though the region is blessed with abundant natural resources for industrial development and social development, they have not been utilised to their full potential <sup>[7]</sup>.

#### 5. FINDINGS

##### 5.1 Interaction with the farmers of Hmarkhawlien, Cachar, Assam

The interaction took place at the Pineapple Farmers Community, a community formed by the pineapple growers of the region. There were a total of 18 farmers with whom the interaction took place. Following points were highlighted during the interaction:-

- Most of the plantations were around 20-25 years old.
- New plants were planted only if a plants dies or in case of expansion.
- Every year a huge quantity of the produce is wasted in peak season because of the lack of storage facilities.
- The farmers want advice on how to 'sell' more instead of how to 'grow' more.

- e. Most the farmers avoided the trainings camps as there was nothing new in that and whatever improvisation was discussed off, according to the farmers, it could not be implemented practically.
- f. The financial benefits were not availed by most of them as they did not know of the benefits and those who knew they just avoided it as there is a lot of paper work involved in getting the benefits.
- g. Although some of the farmers sell the product by maintaining their own logistics, most of the farmers sell the product to the agents who contact them from time to time as the demand arises.
- h. The agents bring their own transportation medium to ferry the pineapples.
- i. Although the agents do not disclose the location where the pineapples are sent but the farmers wild guesses are Silchar, Aizawl, Hojai and Shillong.
- j. The rates are fixed by the community and the rate for last year was Rs. 8 for the smaller fruit and Rs.12 for the larger ones.

## 5.2 Interactions with the Officials of Government Agencies.

### 5.2.1 North Eastern Regional Agricultural Marketing Corporation Limited (NERAMAC)

Following points were discussed in the interactions with the General Manager (Marketing) and the Marketing Manager of NERAMAC:

- a. Logistics is the major problem in the region and cost expensive too.
- b. Infrastructure development is still at a nascent stage. So there is a need to "Make North-East" before "Make-in-North-East" can actually happen.
- c. The schemes of central government do not fit-in with the schemes that are required in the North-Eastern India. The North-Eastern region needs a customised plan in accordance to the specific requirement of the region as the region is different from rest of India.
- d. The plantations are very old and hence quality is deteriorating every year which is further reducing the marketability of the product.
- e. There is a huge demand-supply gap.
- f. The availability of packaging materials is an issue in the region. The packaging materials have to be procured from outside the region e.g. Kolkata.
- g. The organization last sold Pineapple to Dabur almost 6 years back.
- h. The Pineapple processing unit set up by NERAMAC is outlived and hence it needs additional funds so that it can be upgraded. It has also requested for commissioning of a new fruit processing plant in Cachar district which is pending with the Central Government. Apart from that nothing is

done to promote the marketing of pineapple and its associated products.

### 5.2.2 Assam Industrial Infrastructure Development Corporation (AIIDC).

Findings from the interactions with the Managing Director, AIIDC are:

- a. He pointed out that there are various schemes both from the Central as well as the State Government for the improvisation of the industrial infrastructure.
- b. A Mega Food Park, commissioned on 2008, is coming up at Tihu. The Mega Food Park would have primary processing centres which will be supplemented by various collection centres.
- c. Apart from that, many processing plants are beginning to come up in the private sector as well in many other parts of the state.
- d. He also highlighted that in case of pineapple processing the department has received no interest so far and there is very negligible amount of processing of pineapple that is happening at present.
- e. Overall, the department is working very well to meet up to the expectations of the people.

### 5.2.3 Agricultural and Processed Food Products Export Development Authority (APEDA).

Following points were discussed in the interaction with the Regional Manager:

- a. APEDA is involved only in exports of agriculture products.
- b. For export there is a definite procedure involved which most of the farmers fail to comply with.
- c. No information on major trade proceedings with Bangladesh.
- d. There is only one reefer truck to cater the entire North Eastern region.

## 5.3 Interactions with Purbanchal Food Products, Silchar, Assam

The following points were highlighted in the conversation with the proprietor:

- a. The pineapples are procured directly from the growers of Lakhipur sub-division. If the growers fail to supply, procurement is directly made from local wholesalers.
- b. Pineapple Juice and Jam are the Pineapple products.
- c. The sales market is mainly in the state of Mizoram, apart from that the products are sold in the local market also but with less quantity.
- d. Previous year, the peak season sale was around 4000 bottles of pineapple juice every day. No requirement of cold storage is felt as the shelf life is 1 year (approx).
- e. Problems faced are mainly infrastructure issues and unavailability of skilled manpower as well as packaging materials.



f. The employees are to be hired from outside the region by paying high salaries.

#### 5.4 Interaction with Shreedhar Apex Biotech, Baghbahar, Assam

M/s. Shreedhar Apex Biotech is the only tissue culture lab in the area. The firm was approached to know the role it can play in developing the pineapple market of the region. During the course of interactions, following points were discussed and highlighted:

- a. The firm approached some of the NGOs for pineapple production by forming a Farmer Producer Organisation but no one was interested in it.
- b. The producers want a guarantee that the product would be purchased by them and accordingly they wanted the monetary benefit even before plantation.
- c. Tissue culture does not affect the taste or size of the fruit. In fact, it enhances the quality of the product.
- d. A minimum productivity of 40,000 kg of fruit per hectare can be guaranteed, yet no one seems to be really interested.

Pineapple is a bulky product with high volume and low unit price. It also has low shelf life even if it is stored in cold storage units. Hence, construction of just cold storages will not support in adding value to it.

#### 6. OBSERVATION

The overall observation of the study are:

- a. The pineapple producers are dissatisfied as because they feel that they are not getting the expected profits.
- b. The education level is low and hence they refrain from the adoption of modern technologies.
- c. The farmers trust the NGOs more than the Government officials but the NGOs are busy in filling their own pockets.
- d. The farmers are shifting from pineapple cultivation to rubber plantation as it is less labour intensive and it generates greater profit margin.
- e. There is absolutely no value addition at the farm-gate level.
- f. The farmers are not interested in any training camps which teach them to increase the productivity as they are unable to sell the produce which they are producing at present. Their demand is to get a way to sell more.
- g. Almost 20% of the produce is exported to Bangladesh 'unofficially'.
- h. Negligible presence of food processing units for value addition for the pineapples produces of the region.
- i. The interaction between the farmers and officials is very low. Also the number employees in the designated government offices are less.
- j. The procedures involved in getting benefits are quite troublesome for them and hence proper utilisation of the various schemes is not happening practically.
- k. The intentions of all the stakeholders of the system are not focused.

- l. Lack of modern logistics infrastructure.
- m. Unavailability of skilled manpower.

#### 7. CONCLUSION

There is a substantial production of pineapple in the North Eastern Region of India. The producers are not interested in increasing their productivity because they are unable to get the appropriate price for their produce. On the other hand, the food processing industry is not growing because of various issues such as infrastructure, logistics, warehousing and cold storage facilities, etc.

The food processing industry presents a very large opportunity to every stakeholder. This is primarily driven by a robust consumer demand, the changing nature of the Indian consumer, who is more informed and willing to try new products; and the strong production base. Also, the several gaps in the current production and delivery systems actually present a huge opportunity for the growth of companies willing to bet long term in this sector.

The region has the potential to become the horticulture hub of the country but then there is a need to co-ordinate the efforts of all the stakeholders who are responsible and can play a vital role in developing the North Eastern Region as a horticultural hotspot. The food processing industry presents a very large opportunity to every stakeholder. This is primarily driven by a robust consumer demand, the changing nature of the Indian consumer, who is more informed and willing to try new products; and the strong production base. Also, the several gaps in the current production and delivery systems actually present a huge opportunity for the growth of companies willing to bet long term in this sector.

The growth of food processing companies has been sub-optimal because of high cost, low level of productivity, high wastage and lack of competitiveness of Indian food products in the global market. Therefore, to fully leverage the growth potential of the sector, current challenges that are being faced by the industry need to be properly addressed and steps need to be taken to remove the bottlenecks hampering the growth.

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