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STUDIES ON SODIUM DIETHYL DITHIO CARBAMATE FOR REMOVAL OF HEAVY METALS FROM ELECTROPLATING INDUSTRY, WASTEWATER AND USE OF ITS PRECIPITATE AS A DISEASE MANAGEMENT SYSTEM ON PLANTS.

DR SUSAN VERGHESE .P

Associate Professor, School Of Chemical Sciences, Department of Chemistry, John's College, Agra, India

*Corresponding Author: susan.jaison@yahoo.com

Introduction

Rapid urbanization , industrialization and population growth resulted to a generation of large quantities of waste water. Increased discharge of industrial and domestic waste water in receiving bodies and simultaneously increased withdrawal of fresh water make it impossible to rely on the self purifying capacity of those receiving bodies . Decreasing assimilative capacity of water bodies, need for water conservation and growing public awareness in the maintenance of clear environment bring the need for development of appropriate , cost effective and resource recovery based waste water treatment system. Its not possible to achieve, zero waste discharge, but it is essential to treat the waste.

Present era of industrialization and development also brings some fall backs which need immediate attention to overcome their effects on living beings and the ecosystem. One of these is release of toxic heavy metals bearing industrial effluents, which has become a primary challenge for last few decades . The term heavy metals refer to any metallic chemical element that has a relatively high density and is toxic or poisonous at low concentration. In other words heavy metals are chemical elements with a specific gravity that is at least five times the specific gravity of water; the specific gravity of water is one at 4 °C.

The group of transition and post transition elements are referred to as heavy metals these include metals like Hg, Cd, Pb, Cu, Mn, Zn, and Fe. They are natural components of earth's crust. They cannot be degraded or destroyed .As trace element ,some heavy metals e.g.

Cu, Zn, Se are essential to maintain the metabolism of the human body. However, at higher concentration they can lead to poisoning. Heavy metals are dangerous because they tend to bioaccumulate. (Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical's concentration in the environment). Compounds accumulate in living beings anytime are taken up and stored faster than they are broken down (metabolized) or excreted.

Where do they come from? [Sources]

Sources of metals in the water environment can be divided in to two main categories: those that originate from human activities and those of natural origin. The term applied to the former category is anthropogenic ..However during the recent past the amount of heavy metals released to aquatic environment by man made activities have surpassed the amount released by natural weathering .There are over fifty elements that can be classified, seventeen of which are considered to be both very toxic and relatively accessible. Toxicity levels depend on the type of metal, its biological role and type of organisms that are exposed to it, Agency For Toxic Substances and Disease Registry (ATSDR)). Waste water from industries like electroplating, dye, metal finishing, etc contain higher concentration of heavy metals.

The changing characteristics of waste water due to discharge of many contaminants from industries such as electroplating, oils and paints , tanning, distillery etc pose a threat as the waste water usually dumped into

natural water resources like rivers, lakes, ponds, etc and makes the same unfit for human, animal and plant consumption, as well as for industrial use. Plating industry waste water contains, various heavy metal pollutants which depend on type of bath compositions and type of electroplating processes used. The presence of these compounds may impart colour to the water. The dark colour affects the photosynthesis action. These may be toxic and affect the flora and the fauna of the streams. Human consumption of coloured water due to metallic ions leads to dreaded diseases. Metal ions are generally non-degradable. They build up their concentrations in food chains to toxic levels. Mercury, lead, cadmium, silver, nickel, and chromium are very toxic. Among metal ions, Cadmium, silver, nickel, chromium, lead is widely used in electroplating industry. All these metals have severe adverse effects on health of humans and animals.

Excess of copper (470mg) in human body is toxic and causes hypertension, sporadic fever and uremia, pathological changes in brain tissue, coma and even death. Excess of silver (100mg) in human body causes changes in gastroenteritis, diarrhoea, fall of blood pressure and decrease in respiration. Barium toxicity (more than 100mg) causes excessive salivation, tremors, muscular paralysis and paralysis of nervous system. Magnesium toxicity (more than 400mg) causes nausea muscular weakness and paralysis in humans and mammals. Cadmium toxicity (50mg) causes vomiting diarrhoea, abdominal pains, loss of consciousness also causes impaired kidney functioning, impaired reproductive function, hypertension and tumor formation. Lead toxicity (more than 500mg) causes mild anaemia, brain damage, convulsions uncoordinated body movements, eventually producing, coma and death. Hexavalent chromium (more than 70mg) is very toxic, it causes cancer, gastrointestinal ulceration and affects the central nervous system.

Review of Literature

International and National Status

The electroplating bath composition for copper cyanide plating consists of copper cyanide, sodium carbonate, sodium hydroxide, and Rochelle salt and for gold cyanide the bath composition is metallic gold sodium phosphate and potassium cyanide. The electroplating bath composition for iron and silver is ferrous sulphate, ferrous chloride, ferrous fluoborate, ammonium chloride, calcium chloride, boric acid, potassium or sodium cyanide, potassium or sodium carbonate, potassium hydroxide, potassium nitrate and carbon disulphide respectively.

The electroplating bath composition for chromium consists of chromic acid, sulphuric acid, and fluoride catalyst. The electroplating bath composition for

cadmium cyanide and cadmium fluoborate plating processes is cadmium cyanide, sodium cyanide, sodium hydroxide, cadmium oxide, cadmium fluoborate acid, boric acid, ammonium fluoborate, respectively. The electroplating bath composition for nickel and nickel acid fluoride, nickel sulphate, nickel chloride, nickel fluoborate, boric acid, phosphoric acid, phosphorus acid, and nickel chloride; hydrofluoric acid, citric acid, sodium lauryl sulphate respectively. For black nickel plating, the bath composition is the nickel ammonium sulphate, nickel sulphate, ammonium sulphate and zinc sulphate and sodium thiocyanate.

Cyanide is produced on a large scale for use in electroplating and the waste water generated by these industries contains cyanide complexed with heavy metals (copper, nickel, zinc, cadmium, chromium, silver and gold etc.) of variable stability and toxicity. Since cyanide is an inhibitor of the cytochrome oxidase the prevalent water pollution control laws in most countries require its complete removal from streams before discharge. The most commonly adopted method for the treatment of cyanide contaminated effluent is alkaline chlorination oxidation process. It is not effective for nickel and silver cyanide complexes due to slow reaction rates. Other physio-chemical methods such as copper catalysed hydrogen peroxide, oxidation, azonation, electrolyte decomposition etc, are used for treatment of metal cyanides. There are reports on the treatment of metal cyanides using microorganisms. Biosorption of metal cations have been studied extensively by several researchers. Removal and/or recovery of dissolved salts can be done by using technology like hydroxide precipitation, sulphide precipitation, ion exchange, membrane filtration, insoluble starch xanthates, peat adsorption, carbon adsorption, and electrolyte recovery and high pH precipitation. The recovery of process bath can be accomplished by electro dialysis method.

Removal of organics from plating industry wastewater can be done by aerobic decomposition, carbon adsorption and resin adsorption. Oil removal can be achieved by centrifugation, coalescing floatation, skimming and ultra filtration methods. Reduction of chromium(VI) from metal finishing and cooling lower blow downs can be done by electrochemical reduction method.

Heavy metals from wastewater can be recycled. Heavy metal ions can be removed by precipitation method. Zinc, cobalt, manganese, iron, mercury, bismuth, silver and arsenic metals present in the electroplating industry wastewater can be removed by precipitation. There are reports of removal of chromium from wastewater by adsorption using low cost adsorbents such as flyash, baggase, wheat straw dust and coconut coir. Wastewater contains heavy metals such as lead, copper, manganese, zinc, iron, cadmium, nickel and chromium were analysed by flame atomic absorption spectrophotometer.

The extensive use of chromium containing compounds in plating industrial processes releases chromium (VI) resulting in the contamination of surface water and soil. Though the chromium is an essential nutrient for plant and animal metabolism, however when accumulated at higher concentration it causes serious disorders and diseases and it can ultimately become lethal (Bhalke et.al., 1999). In plating industrial wastewater mostly, the chromium is found in two forms. One is hexavalent and the other is trivalent, where as the hexavalent form is more common and hazardous to biological activities. At high concentrations, all the compounds of chromium are toxic. Exposure of human beings to the chrome bearing dust for longer period will cause skin irritation and corrosion of skin, ulcer formation, liver damage, respiratory tract infection, nausea, vomiting, severe diarrhoea, epi gastric pain and hemorrhage. The removal of chromium can be done by using methods such as chemical precipitation, electrochemical reduction-exchange, evaporation and concentration, electrolysis and electroplating, ion floatation reverse osmosis activated carbon adsorption etc. Though activated carbon is an ideal adsorbent for the removal of chromium; its high cost prohibits its application in the wastewater treatment, regeneration cost itself is very high and may not be economically feasible for the wastewater treatment general.

Various adsorbents were used for the removal of hexavalent chromium which include activated carbon, activated carbon developed from fertilizer waste, rice husk carbon, waste tea leaves carbon, brick kiln ash, baggasey and coconut coir carbon, sawdust, bituminous coal, low cost adsorbents such as baggasey and coconut coir. Chemically activated sawdust is found to possess greater adsorption, efficiency, for all metals than rice husk under identical experimental conditions. The aquatic plants can concentrate heavy metals 1000-20000 times their concentration in water. Some of the plants used for this purpose are ceratophyllum, lemna, spirodela, pistia, elodea etc, but the most outstanding and promising plant has been water hyacinth. The plants can be grown in the wastewater for a shorter or longer period. The resultant crop is harvested; some plants are left to grow further. The system is simple and less expensive. The harvested plants can be put to several profitable uses.

There are numerous reports documenting the capability of pure cultures of bacteria, algae and fungi, to remove heavy metal ions from solutions, multi species communities of bacteria remove silver equal to 32% of the dry cell weight inorganic and biological sorbents were used to remove Pb²⁺ from wastewater.

The heavy metal dithiocarbonates can be used as pesticides. The pesticides like mancozeb, maneb, ferbam, zeneb and ziram can be used to control broad range of plant diseases. Conventional chemical treatment methods including ion exchange precipitation,

filtration, oxidation, reduction, electrochemical recovery, membrane separation, and other techniques maybe ineffective or uneconomical when the heavy metal ion concentration in the polluted environment are in the range of 10-100 mg/litre. There is an immediate need to introduce cleaner technologies in electroplating industries to minimize the pollution and to protect the degrading environment. It is not possible to achieve zero waste discharge but it is essential to treat the waste or recycling of the heavy metals produced in the waste of plating industry.

The present study is of utmost importance and significance as it draws the attention towards the problem of heavy metal contamination in drinking water from rivers, lakes and ponds, etc which are very toxic and hazardous to human life and flora and fauna. Toxic metals change the biological structures and symptoms into inflexible and irreversible conformation leading to deformity in the body or finally death.

Almost all metals are toxic at higher concentrations and some are lethal even at very low concentrations although heavy metals within limits are essential for aquatic organisms, plants as well as humans to survive and function.

Hence it is proposed to find techniques by which the heavy metals present in electroplating can be removed and to make use of the removed heavy metal complexes as a disease management system on plants.

Objectives

1) To collect and characterize the plating industry waste water for a period of one year (2006-2007) from sampling sites such as (i) B.R., Kinari Bazar, (ii) S.K., Pawan Market, (iii) B.R., Fawara, (iv) V.R., Sabka Bazaar, (v) RFR, Kinari Bazaar.

2) The assessment, development and application of processes in various seasons (winter, summer, post monsoon), for waste water depend on a detailed knowledge of the composition of the wastewater, this knowledge can be obtained only by the proper application of suitable analytical methods. These methods are

- i. pH by pHmeter
- ii. Biochemical Oxygen Demand (BOD) by titration method
- iii. Chemical Oxygen Demand (COD) by titration method
- iv. Heavy metals (Cu, Mn, Ni, Pb and Zn) by using atomic absorption spectrophotometry

3) The precipitation of heavy metals with sodium diethyl dithio carbamate

4) Application of heavy metal diethyl dithio carbamate as disease management substance.

5).To suggest other waste water control measures to reduce/nullify the pollution characteristics to ensure safe environment promote and maintain highest standard of physical mental and social well being of the citizens

Methodology

The physical examination

- i. Colour
- ii. Odour
- iii. Turbidity

Will be investigated on the spot of collection of wastewater. Digital turbidity meter will be used to measure the turbidity.

The chemical examination

- i. pH measurement using digital pH meter and
- ii. Total solids by gravimetric method.

The measurement of pH gives an idea about whether the water is acidic or alkaline in nature.

Measurement of biochemical oxygen demand (BOD)

By titration method.The BOD is the amount of oxygen required by bacteria while stabilizing decomposable organic matter under aerobic conditions.

The decomposition of organic impurities in presence of bacteria while stabilizing decomposable organic matter under aerobic conditions.

The decomposition of organic impurities in presence of bacteria results in utilization of a part of the dissolved oxygen by the bacteria during their respiratory and metabolic activities. This depletion of oxygen is considered as a measure of the strength of water.

Measurement of chemical oxygen demand (COD) will be done by titration method .COD is used to measure the pollution strength of waste water. Most of the organic compounds can be decomposed to carbon dioxide and water by the action of strong oxidising agents regardless of the biological assimilability of the substances.

Investigation of heavy metals viz.[He, As, Cu, Mn, Fe, Ni, Pb and Zn] by atomic absorption spectrometer(AAS). With the help of AAS, one can investigate the concentration of heavy metals in electroplating wastewater.

Complexation of heavy metals present in wastewater by sodium diethyldithiocarbamate.

Investigation of this heavy metal diethyldithiocarbamate as a disease management system on vegetables,

Experimental

Collection of samples:

Grab samples of waste water from electroplating sites before their mixing into the drainage system were collected from the five mentioned sites-

1. B. radium [AB-1]
2. S. radium [AB-2]
3. Br. radium [AB-3]
4. V radium [AB-4]
5. R.F radium [AB-5]

In plastic bottles of one litre capacity for specific parameters.

Labeling of samples:

Samples from each site is labeled with

1. Site name
2. Date of collection
3. Time
4. Sample No:

Colour and odour are noted at the time of collection. Conductivity and pH within 2 hours from collection upon lab arrival.

Chemical properties, health effect, environmental effects of each Cu, Fe, Mn, Ni, Pb, and Zn, metal and observed concentration and comparison of the above metals during one year ,monitoring of waste water from electroplating sites AB-1, AB-2, AB-3, AB-4, and AB-5 of Agra city in order to asses the metal pollution load in effluent from these shops has been discussed further in this chapter.

Summary

The generation of heavy metals in electroplating industry is through the following processes. Collection of liquid waste in a collection tank: the capacity has to be calculated based on total maximum waste generated plus some spare capacity say 25-50%. Settlement of suspended solids: By coagulation and flocculation by addition of alum plus polyelectrolyte. Chemical reaction: For removal of metals by precipitation, chemicals have to be added as discussed earlier.Mixing of the chemicals in the waste either by flash mixing or by compressed air circulation. Sludge withdrawal over sludge drying beds having suitable filter media. Withdrawal of settled treated effluent from the reaction tank in to pH tank. Checking the pH and adjusting the same permissible limit by adding sulphuric acid.. Disposal of the final treated effluent in to nearby sewer manhole/opendrain.. Filtrate return from sludge drying bed back in to the collection tank.Removal of semidry sludge from the drying bed for complete drying separately and final disposal through

municipal garbage removal system.. Dual media filter for further reduction in suspended solids by filtration.

. Activated carbon filter provided for further reduction in copper and cyanide by the method of adsorption. For many years, attention has been devoted to the development of methods for removing heavy metals from wastewater arising from industrial operations. The most common methods for removing heavy metals have involved chemical precipitation, ultra filtration, solvent extraction, electrodeposition, biological treatment, ion exchange and adsorption. Waste water from industries like electroplating, dye, textile, metal, engineering and pesticides etc contain higher concentration of heavy metal. Plating waste water containing heavy metal at levels that might be considered hazardous to environment could pose risks to public health. The survey of literature of our present work is in agreement that several studies have been done on removal of heavy metals or on technologies for heavy metal removal from industrial waste water and less has been done to recycle or reuse these heavy metal present in waste water which after removal will create otherwise disposal problem.

Present research includes the recovery of heavy metal present in waste water from electroplating industry and utilization of these metals in synthesis of carbamate pesticides (fungicide) and application of these in controlling fungal diseases of vegetables (potato, tomato, brinjal and okra) and ornamentals (rose and sunflower). Grab samples from the electroplating sites were collected in plastic bottles of one liter capacity for specific parameters and were properly labeled with the site name, date of collection, time, sample number etc. The pH, conductivity, acidity, alkalinity, BOD (biological oxygen demand), COD (CHEMICAL OXYGEN DEMAND), and heavy metal (Cu, Fe, Mn, Pb, Ni and Zn) concentration were determined in order to assess the quality of waste water let off from electroplating units. pH and conductivity were measured within two hours from collection of the sample upon laboratory arrival.

The pH is measured with a digital pH meter. The pH values indicate the degree to which waste water samples were alkaline or acidic. Highest pH value was 13.27 for AB-1 sample during period from November to February (Nov-Feb); value indicates high alkalinity of sample water. Such high pH value waste water when mixes with natural water sources like rivers are responsible for its bitter taste. Highly acidic waste water sample was recorded at site AB-2 during November to February, value being 4.16. This was the lowest pH recorded throughout the study. Alkalinity and acidity determined by titration method are in agreement with the value determined by digital pH meter. Thus the highest pH values (13.27) had alkalinity of 2425 mg/l and lowest pH (4.16) had acidity value of 2650 mg/l. Mostly the waste water samples were within the limits prescribed by CPCB 2000, EPA 1987 for pH of waste water

discharged from electroplating industry and IS: 2490-1974 tolerance limits of pH for industrial effluents discharge in to inland surface waters which is 6.0-9.0 (CPCB, EPA) and 5.5 – 9.0 (I: S).

Along with pH, conductance was also one such parameter which was determined for all waste water samples within two hours from collection. The highest conductance (5.01 μ mhos/cm) value was obtained for AB-5 site sample during period between November to February. High conductance indicates that the dissolved solids and salts concentration is high in the water sample analyzed as it is the dissolved salts in water which conduct electricity and pure water does not conduct electricity.

Biological oxygen demand (BOD) is the amount of oxygen required by microorganisms present in water or waste water for converting organic matter in water in to inorganic matter. It can precisely be defined as the rate of removal of oxygen by microorganisms in aerobic degradation of dissolved or even particulate organic matter in water. Since BOD is the index of organic pollution in water, high organic pollution was recorded at site AB-3 indicate by BOD value of 480 mg/l during period between July- Octobers. AB-1 and AB-4 sites during period between July-Oct (54.85 mg/l) and November to February (56.06 mg/l) respectively had low BOD value observed for all sites in all periods exceeded the tolerance limit prescribed by I:S for discharge of industrial effluents in to inland surface waters which is 30 mg/l.

Chemical oxygen demand (COD), measuring the oxygen required in oxidizing the organic compound present in water or waste water by means of chemical reactions involving oxidizing substances such as potassium dichromate and potassium permanganate is also an index for organic pollution, highest COD concentration (580 mg/l) was observed at site AB-4, in period between July-Oct and least COD value was 58.45 mg/l at site AB-4 in a period between March-June. COD values of site AB-5 during March-June, AB-4, AB-5 site during July-Oct, and AB-4 during Nov-Feb exceeded the tolerance limits for COD (250 mg/l) by I: S for discharge of effluents in to inland surface waters.

Copper metal concentration prescribed by CPCB, EPA, and I: S for industrial effluents is 3 mg/l. High concentration of copper causes hypertension, sporadic fever and coma in human. Highest copper concentration was 27.60 mg/l and 3.68 mg/l in site sample AB-5 and AB-4 respectively during Nov-Feb. All other copper concentration values were below the prescribed limits. Iron may cause conjunctivitis, choroiditis and more than 10 mg/lkg level of iron causes rapid increase in pulse rates, congestion of blood vessels, hyper tension and drowsiness. 3.0 mg/l is the waste water discharge standard for iron prescribed by Central Pollution Control Board (CPCB), EPA, and I:S. Highest Iron concentration

was in site AB-2 value being 16.70mg/l during period Nov-Feb. Manganese concentration above 100 ppm is toxic to both man and mammals. Manganese effects occur mainly in the respiratory tract and in brains. It causes growth retardation, fever, muscular fatigue, eye blindness. Waste water discharge standard for manganese prescribed by I: S is 2 mg/l. Highest manganese concentration was in site AB-4 (56.80) during period Nov-Feb. Except the three measured values for manganese concentration, all other values exceeded the limit prescribed by I: S.

Nickel concentration more than 30 mg causes change in muscle, lung, liver, brain and kidney and also can result in cancer. It also causes tremor, paralysis and even death.

Highest nickel concentration (24.92) was in sample of site AB-3 in period between Nov-Feb. Nickel metal concentration prescribed by CPCB, EPA, and I:S for industrial effluents is 3 mg/l. Eight observation values of nickel concentration were above the limit prescribed by CPCB, EPA and I:S. Lead concentrations above 800 mg in humans create toxicity. It causes mild anemia, brain damage, loss of appetite, vomiting, convulsions, uncoordinated body movement and stupor eventually producing coma and death. Lead metal concentration prescribed by CPCB, EPA, and I: S for industrial effluents is 0.1 mg/l. Lead concentration was 1.02 mg/l in site AB-4, in period between Nov-Feb.

Heavy doses (165 mg) of Zinc salts in continuation cause vomiting, renal damage, cramps, nausea and anaemia. Zinc concentration prescribed by CPCB, EPA, and I:S for industrial effluents in 5 mg/l. highest zinc concentration was 12.20 mg/l in site AB-4 in period between Nov-Feb. Five observation values of zinc concentration were the limit prescribed by CPCB, EPA, and I:S.

Results of physico-chemical analysis of waste water reveal that since AB-1 site had the treatment plant, it was least metal polluted among all the sites and its waste water was highly alkaline, with highest organic pollution. AB-2 site waste water was low in metal pollution, acidic in nature with slight organic pollution. AB-3 waste water was equally metal polluted and organically polluted, and slightly alkaline in nature. AB-4 waste water was highest in metal pollution, with low pH value but was not acidic. It was less organically polluted. AB-5 waste water sample was high in metal pollution, alkaline in nature and least in organic pollution. In the lab conditions metal (Cu, Fe, Mn, Pb, Ni and Zn) diethyldithiocarbamate. Metal diethyldithiocarbamate fungicide was synthesized at pH 9.3 and dissolved in mixture of ethanol and water, 7:3 V/V and sprayed through hand held sprayer. For fine coverage of the target plant parts. In study field area the vegetable and ornamental plants have been monitored on every day basis for disease symptoms occurrence. These plants are grown from seeds obtained from

healthy and disease prone plants of tomato, brinjal, okra (bhindi), sunflower and the saplings of healthy and disease prone potato and rose plant. One row in the field is control for the study of field area, in which one plant of all vegetables and flowers is present and this row is not subjected to any spraying. Some outer study area cases were also included for extended study of spraying effect. One plant each of same vegetable and flower were also grown in pots and sprayed for the same reason.

After the analysis of waste water, the study of application of metal diethyldithiocarbamate fungicide which was synthesized under lab conditions was also carried out in study field area, and other disease Scases. Vegetables and flowers selected for the spraying effectivity observation are potato, tomato, brinjal, bhindi (okra), sunflower and rose, respectively. In the field seven rows were dugged, and in each row all the four vegetable plants and two flower plants were grown, first row was not subjected to any metal diethyldithiocarbamate fungicide spray, and other six rows were subjected to one metal diethyldithiocarbamate fungicide spraying each. Second row was subjected to copper diethyldithiocarbamate fungicide when the initial symptoms of disease occurred in plant. Similarly third, fourth, fifth, sixth and seventh row were subjected to iron diethyldithiocarbamate, manganese diethyldithiocarbamate, nickel diethyldithiocarbamate, lead diethyldithiocarbamate and zinc diethyldithiocarbamate respectively.

In case of potato, the two very common fungal diseases Early Blight caused by fungus *Alternaria solani* and Late Blight by fungus *Phytophthora infestans* occurred in the field and outer study area, and were observed for controlled by each metal (Cu, Fe, Mn, Pb, Ni, and Zn) diethyldithiocarbamate fungicide spraying, which was applied at the interval of seven days in humid climate and at fourteen day interval in dry climate. It revealed that copper diethyldithiocarbamate was found effective in cure of Early Blight disease and Zinc diethyldithiocarbamate in control of Late Blight of potato. In case of tomato, fungal disease observed in the study field area were Buckeye Rot caused by fungus *Phytophthora parasitica*, Early Blight disease caused by fungus *Alternaria solani* and Late Blight caused by fungus *phytophthora infestans*. The study revealed the effectivity of copper diethyldithiocarbamate in cure of Buckeye Rot and Early Blight disease of tomato and Zinc diethyldithiocarbamate in control of Late Blight of tomato. In brinjal, fungal disease occurred in study field area was Leaf Spot caused by *Cercospora melongenae* and Phomopsis Blight caused by *Phomopsis vexans*. Manganese diethyldithiocarbamate was effective in curing the Phomopsis Blight of brinjal.

In case of okra, fungal disease occurred in study field area were Cercospora Leaf Spot caused by fungus *Cercospora abelmoschi*, Damping Off by *Pythium* spp., *Rhizoctonia* spp., and Powdery Mildew by *Oidium* sp. Manganese diethyldithiocarbamate successfully cured Damping Off disease and none other diseases of okra

(bhindi) was controlled by any of the fungicidal spray . Fungal disease of sunflower which occurred in study cases were Sclerotinia Wilt caused by fungus *Sclerotinia sclerotiorum*, Leaf Spot caused by *Alternaria helianthi*, *Alternaria zinniae*, and Rust caused by *Puccinia helianthi* Schw. It is , confirmed, that copper diethyldithiocarbamate was an effective control for the Leaf spot of sunflower diethyldithiocarbamate for Rust disease.

In case of rose flower plant , disease observed in study area were powdery Mildew caused by fungus *Sphaerotheca pannosa var.rosae*, Black Spot caused by *Diplocarpon rosae* and Rust caused by fungus *Phragmidium* spp. The results showed that metal diethyl dithiocarbamate were effective for all the disease which occurred. Zinc diethyldithiocarbamate emerged as a perfect cure for powdery Mildew, iron diethyldithiocarbamate was effective for Black Spot control and manganese diethyldithiocarbamate was effective against Rust disease of rose flower plant.

It is therefore, concluded that metal diethyldithiocarbamate worked as an effective fungicide in control of fungal disease of vegetables and ornamentals which have great consumption and market value in india and abroad. Among the fungicide synthesized (copper diethyldithiocarbamate, iron diethyldithiocarbamate, manganese diethyldithiocarbamate, nickel diethyldithiocarbamate, lead diethyldithiocarbamate, zinc diethyldithiocarbamate), copper diethyldithiocarbamate effectively emerged as cure for Early Blight of Potato, Buckeye Rot and Early Blight of Tomato and Leaf Spot of sun flower. Iron diethyldithiocarbamate was

effective against Black Spot disease of rose, Manganese diethyldithiocarbamate was an effective cure for control of Phomopsis Blight of brinjal, Damping Off disease of okra and Rust disease of rose flower plant. Zinc diethyldithiocarbamate was effective in control of Late Blight of potato. Late Blight of tomato, Rust disease of sunflower and powdery mildew of rose flower plant.

All the metal diethyldithiocarbamate (copper diethyldithiocarbamate, iron diethyldithiocarbamate, manganese diethyldithiocarbamate and zinc diethyldithiocarbamate) which were found effective in curing one or more fungal diseases of potato, tomato, brinjal, bhindi (okra), sunflower and rose are contact fungicide as they remain on the surface of plants. They are protectants and work by contact action on the surface of the plant to which they have been applied. Repeated applications are needed to protect new growth of the plant and to replace material that has been washed of by rain/irrigation. These contact fungicides have multisite activity and thus are active against more than one point in metabolic pathway in a pathogen and can work against more than one critical enzyme needed by the fungus for its growth.

According to FRAC (Fungicide Resistance Action Committee) since diethyldithiocarbamate are contact and multisite in activity they have low risk to resistance development problem. It is, observed, that effect of metal diethyldithiocarbamate fungicide applied for disease control in our study is in agreement with effectivity of other dithiocarbamate fungicide like ferbam, mancozeb available in market for application in agriculture and home garden practices.

Table & Figure 1: Nickel metal concentration in mg/l

S.No	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	1.67	0.04	7.29
2	AB-2	3.34	0.13	16.4
3	AB-3	2.16	2.03	24.92
4	AB-4	3.36	1.24	12.60
5	AB-5	4.20	1.52	19.14

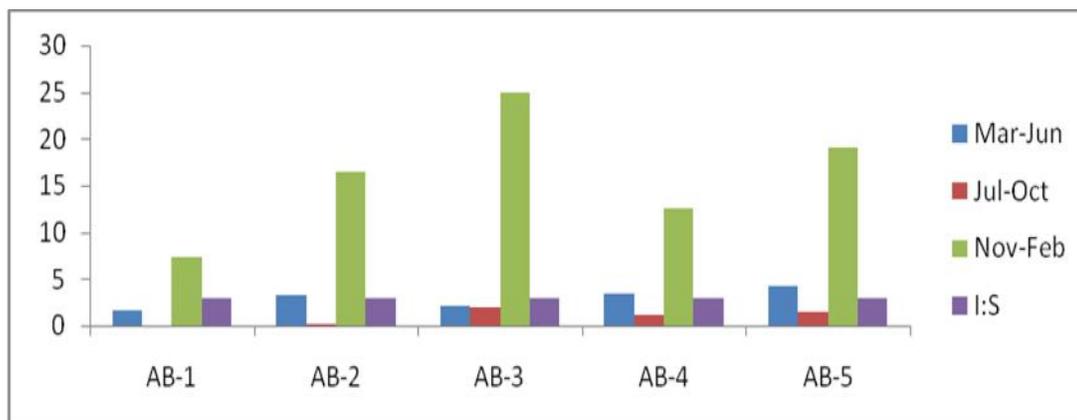


Table & Fig 2: Lead metal concentration in mg/l

S.No	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	N.D	N.D	0.03
2	AB-2	0.15	N.D	0.20
3	AB-3	0.62	N.D	0.01
4	AB-4	0.06	N.D	1.02
5	AB-5	0.08	N.D	0.85

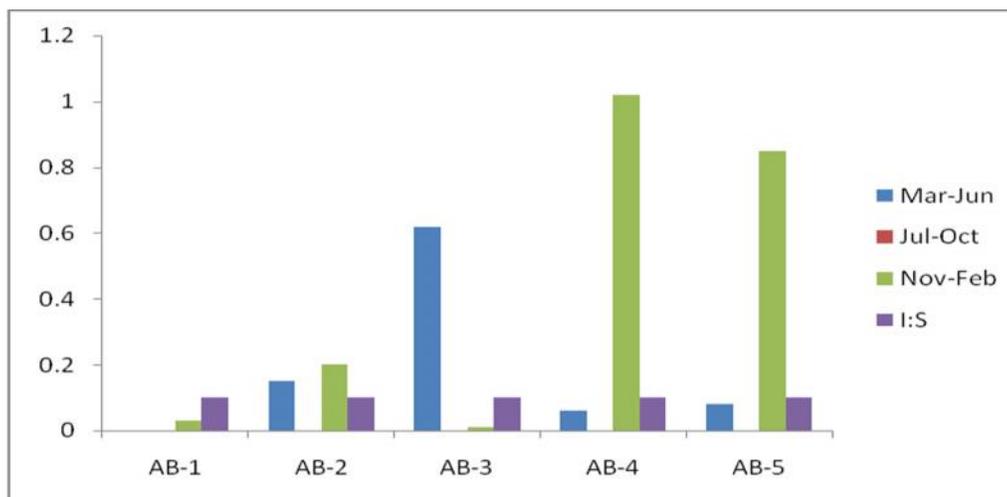
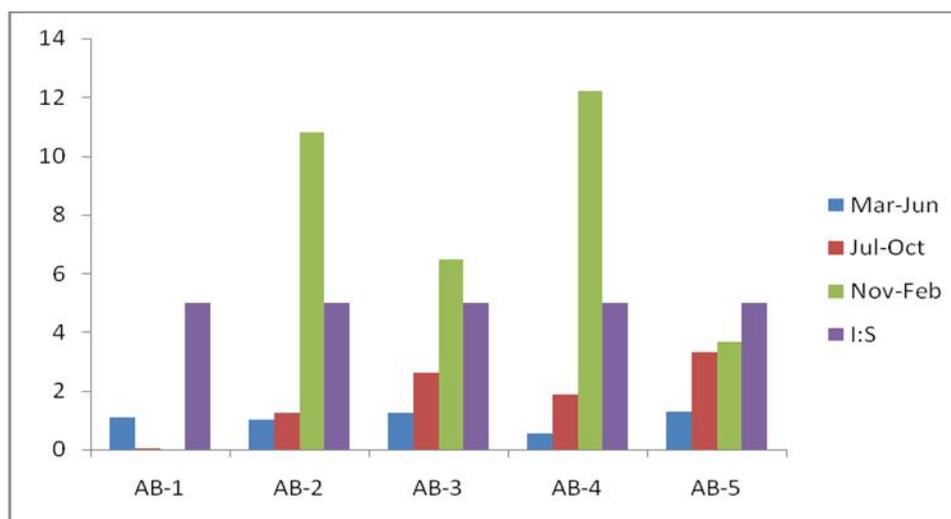


Fig 3: Zinc metal concentration in mg/l

S.No	Sites	Mar-Jun	Jul-Oct	Nov-Feb
1	AB-1	1.08	0.05	0.01
2	AB-2	1.0	1.23	10.79
3	AB-3	1.25	2.61	6.46
4	AB-4	0.54	1.89	12.20
5	AB-5	1.27	3.32	3.68



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