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DETERMINATION OF HEAVY METAL CONCENTRATION AND PHYSICO-CHEMICAL PROPERTIES OF SELECTED PAINT FACTORIES EFFLUENTS AND THEIR IMPACT ON THE GERMINATION AND GROWTHS OF VEGETABLES

BY

MEKWANINT REBUMA

A Thesis Submitted To African Center Of Excellence For Water Management (Acewm) / Addis Ababa University (AAU) In Partial Fulfillment Of The Requirements For The Degree Of Master Of Science In Water Management Specialization In Water Quality Management

SEPT, 2021

ACEWM/AAU, ETHIOPIA

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ADVISOR THESIS SUBMISSION APPROVAL SHEET

SCHOOL OF GRADUATE STUDIES

AFRICA CENTER OF EXCELLENCY FOR WATER MANAGEMENT

ADDIS ABABA UNIVERSITY

This is to certify that the thesis entitled "**Determination of Heavy Metal Concentration and Physico-Chemical Properties of Selected Paint Factories Effluents and Their Impact on the Germination and Growths of Vegetables**'' submitted in partial fulfillment of the requirements for the degree of Master of Science with specialization in Water Quality Management, the Graduate Program of the Water management and has been carried out by Mr. Mekwanint Rebuma under my supervision. Therefore, I confirm that the student has fulfilled the requirements and hence hereby can submit the thesis to the department for defense.

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Dr. Yonas Chebude

(Advisor)

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Date

DECLARATION

I, Mekwanint Rebuma declare that the content of this thesis is my original work with the exception of such quotations or references which have been credited to their authors or sources and this thesis has not been previously submitted to this or any other University for a degree award.

Signature…………………

Date………………………

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ABBREVIATIONS AND ACRONYMS

APHA: - American Public Health Association

BDA: -Basin Development Authority

BOD: - Biological Oxygen Demand

COD: - Chemical Oxygen Demand

DO: - Dissolved Oxygen

EFCCC: - Environment, Forest and Climate Change Commission

EC: - Electrical Conductivity

IGAD: - Intergovernmental Authority on Development

AAS: - Atomic Absorption Spectrometry

FAO: - Food and Agriculture Organization

GP:-Germination Percentage

HDPE: - High Density Polyethylene

HM: - Heavy Metal

IPEN: - International Pollutants Elimination Network

PMT: - Photo Multiplier Tube

TSS: - Total Suspended Solids

TDS: - Total Dissolved Solids

TS: - Total Solid

RSC: - Residual Sodium Carbonate

SAR: - Sodium Adsorption Ratio

VOCs: - Volatile Organic Compounds

WHO:-World Health Organization

WWTPS-Waste Water Treatment Plants

ABSTRACT

Effluents from the paint industry have been a major source of environmental pollution. The paint industry generate wastewater, primarily due to cleaning operations of mixers, reactors, blenders, packing machines and floors. There is a need to investigate the compliance of wastewater discharged from paint industries with regulatory standards. In response, this study evaluates the physicochemical parameters of both raw and treated wastewater, the wastewater treatment plants (WWTPs) efficiencies as well as the compliance level of three selected paint manufacturing companies in Addis Ababa, Ethiopia, with some regulatory standards: Ethiopian Standard and World Health Organization (WHO). A study on the impact of a paint industry effluents on the vegetables solanum lycopersicum (tomato) and D. carota (carrot) was also carried out. Analysis of physico-chemical and heavy metal parameters of selected paint factories' samples in Kadisco (CA), Zemilli (ZE), and Nifas Silk (NS) were performed to investigate the concentration of status of the parameter. In this study, physicochemical and heavy metal parameters such as pH, TDS, EC,COD, BOD, PO_4^{3-}, NO_3^-, SO_4^{2+}, NH_3, NH_4^+, Cr^{+6},Zn^{+2}, Cd and Pb of the fourteen wastewater samples were analyzed using, standard methods. The values of pH, electrical conductivity (EC) and total dissolved solids (TDS) levels were in the range of 6.80-8.50, 858.00 - 2540.00 mS/m and 410.00- 1270.00 mg/L, respectively. The range of other parameters include ammonia; 0.35-0.42mg/l, biological oxygen demand (BOD); 6.40 – 35.76mg/L, chemical oxygen demand (COD); 283.00–485.0 mg/L, nitrates; 0.68-12.50 mg/L, phosphate; 1.31-1.52, sulfate; 32.33–188.33 mg/L, lead; 0.01–0.06 mg/L, zinc 0.01-0.02 mg/L while cadmium and chromium were below detection limits. The results indicated that the WWTPs of the studied paint factories were ineffective in reducing the pH, TDS, and EC to acceptable limits. Wastewater samples were collected from two paint factories (Kadisco paint and Nifas Silk paint factory) and their impacts on the germination and growth of (vegetables solanum lycopersicum (tomato) and D. carota (carrot)) have been studied. The obtained results revealed that wastewater from Cadisco paint factory did not affect seed germination except a minor inhibition in solanum lycopersicum (tomato). Effluents from Nifas Silk factory stimulated seed germination in both solanum lycopersicum (tomato) and D. carota (carrot). It can be concluded that paint factories wastewater may have different effects on growth of different vegetables, depending up on the nature of wastewater and sensitivity of a plant species to wastewater.

Key words: wastewater treatment; paint industries; percentage efficiency; germination percentage plant growth

CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF APPENDICES

1. INTRODUCTION

1.1 Background

Water is a major factor and of the highest priority for the existence of human life and crop production(Dennis W. & Robert S., 2019). The pollution of water resources is a global problem ((Özkara et al., 2011); Ohe et al. 2003; Monte Egito et al. 2007). Industrial effluents are a main source of direct and often continuous in- put of pollutants/toxicants into aquatic ecosystems with long-term implications on ecosystem functioning (Odeigah and Osanyinpeju 1995; Chan et al. 2003; Lah et al. 2004; Smolders et al. 2004; Samuel et al. 2010).The paint industry is one of the industries that causes water pollution and generates wastewater primarily due to cleaning operations of mixers, reactors, blenders, packing machines and floors. (Berihun,et.,al 2020). Using different chemicals, such as binders, solvents, non cellulose thickeners, latexes, emulsifying agents, inorganic pigments, dyestuffs, extenders, cellulose pigment and additives, wastewater contains appreciable concentrations of carbon BOD, COD, suspended solids, toxic compounds (toxic heavy metal compounds) and colored materials (Jesionowski and Ciesielczyk, 2013) (Dey, B.K., 1999).

The Zemilli paint factory in Addis Ababa, Ethiopia produces a maximum of 36,000 liters of paint per day and as a result it generates about 500 liters of liquid waste on average per day and the others also generates high amount of liquid wastewater. In Ethiopia there are more than 22 paint factories(Berihun & Solomon, 2017a). Most of them are located in Addis Ababa in different parts of the sub- city, some of them are concentrated in residential and commercial areas in Addis Ababa. They have no proper wastewater discharging mechanism and no modern treatment plants which can handle their effluent waste accordingly (Berhun et.al 2020). All these industries produce various effluents that are discharged into the nearby water body. (Hajihashemi et al., 2020) It is widely known that in many low-income nations, industrial and environmental standards are non-existent, and where they are available, the mitigation instruments are inefficient. This is mainly due to lack of reliable and extensive monitoring system for industrial emissions as well as enforcement of compliance with the industrial standards (Aniyikaiye et al., 2019). The discharge of such wastewater into the environment causes a serious problem of contamination of water bodies, thereby damaging the resident aquatic animals and plants(Moore & Moore, 1976). The polluted water causes several diseases in animals and humans, water bodies contributes toward the contamination and destruction of aquatic habitats and the water becomes unsuitable for aquatic biota as well as adversely affecting soil quality and crop yields (Azizullah et al. 2011; Heikens 2006; Khan et al. 2002)(Olowu et al., 2010) .

In many developing countries of the world including Ethiopia, wastewater is directly used for irrigation(NAND SINGH et al., 2012). Wastewater is a complex mixture of nutrients and toxic chemicals and can reduce germination rates, decrease the water potential of plants, inhibits photosynthesis, and reduces growth of crops (All et al., 2015)(Kirkham, 1990). Most of the studies show that properly untreated effluents can be harmful to plants, due to the higher pH, TDS, salinity and various toxic substances present (Uwah, 2015)(Abrha & Chen, 2017). Industrial wastewater including paint industry usually carry a heavy load of toxic metals such as Cd, Cu, Cr, Ni, Pb, and Mn, which can adversely affect crop growth and yield(Ahmad, 2015) (Aslamet al. 2004; Yadav et al. 2002; Luo et al. 2012). High concentrations of heavy metals restrict various physiological and metabolic processes in plants (Ahmad et al. 2011). They also decrease plant growth that can be induced by disruption of photosynthesis or mineral nutrient imbalance, which causes a decline in yield(Mosse et al., 2010). The characteristics of paint industries effluent and impact of paint factories wastewater on vegetables growth has rarely been studied in the country. Therefore, this study aims at determining levels of heavy metal contaminants and other physicochemical properties of effluents being discharged from paint manufacturing industries into the environment and compare the levels with the Ethiopia’s and WHO’s standards, and evaluate the effect of industrial wastewater on two commonly grown vegetable species in Ethiopia, i.e. Solanium lycopersicum (tomato) and D. carota (carrot). Wastewater samples were collected from selected paint factories and their effects on various parameters including seed germination, root and shoot length were evaluated.

1.2 Statement of the Problem

As many researches indicated, paint industry discharge considerable amounts of chemicals and heavy metals in their wastewaters(Aniyikaiye et al., 2019). Many of these chemical compounds in the effluent degrade the normal characteristics of water by reducing the oxygen level and changing the composition of existing heavy metals and other organic constituents (Jolly et al., 2013). Wastewater management is an inherent aspect of many industrial operations and according to the guidelines and standards for industrial pollution control in Ethiopia, all discharges of effluent with constituents beyond the specified limits into public drains, streams, rivers or underground injection are unacceptable (EEPA, 2010)(Berihun & Solomon, 2017a). in Ethiopia The efficiency of the treatment plant for treating paint factories wastewater was not studied yet. Therefore, it is mandatory for these paint factories to evaluate the efficiency of their wastewater treatment system. To promote this, understanding of the physicochemical and biological constituents found in the paint wastewater play a major role. Besides, understanding of the nature and characteristics of wastewater is also important in the design and operation of wastewater treatment, and reusability of the wastewater. Therefore knowing the characteristics of the wastewater of paint factories is crucial. It is also reported that surface water bodies in developing countries are under serious threat as a result of indiscriminate discharge of polluted effluents from industrial, agricultural, and domestic activities (Kambole, 2003).

Water bodies like rivers, ponds, lakes especially in the Upper Awash tributaries are polluted with toxic heavy metals and chemicals that come from untreated urban, agricultural and industrial effluents(Y & M, 2018). Paint industries are one of the consequences to contaminate those rivers. However, although these wastes are basically polluting and contaminating the above mentioned water resources, the sediments in downstream of the rivers are used by the residents for growing of different vegetables(Y & M, 2018). It may result in bioaccumulation of heavy metals in humans using water directly and eating agricultural products (vegetables and crops). The consumption of vegetables irrigated with wastewaters of domestic and industrial origin poses a serious risk to public health. Seed germination and crop growth are an important phase that ensures reproduction and crop productivity. Therefore it is essential to determine the effect of paint wastewater on germination and growth of the vegetables. Few research works have been undertaken on the assessment of the physicochemical and heavy metal toxicity from effluents of paint factories in Addis Ababa (Industries, 2019)(Berihun & Solomon, 2017a). However the reports have not yet studied the efficiency of the waste water plant and effect of waste water. Therefore, this study aims to determine heavy metal concentration and physicochemical properties of effluent of paint factories and efficiency of wastewater treatment plants. Moreover, it investigates the impact of wastewater on the germination and growth of vegetables.

1.3 Objective

1.3.1 General objective

The general objective of this study is “Determination of heavy metal concentration and physicochemical properties of effluent of paint factory and its impact on the germination and Growth of vegetables.”

1.3.2 Specific objectives

- To determine the level of heavy metal concentration and characterize physicochemical properties of discharged waste water from paint industry
- To evaluate the efficiency of waste treatment plant of each paint industry and compare the results with internationally set limits (WHO standard) and ES (Ethiopian standard).
- To study the effects of paint factory waste water on seed germination and growth of solanum lycopersicum (tomato) and D. carota (carrot).

1.4 Research Questions

- ➢ What is the status of heavy metals (Cd, Pb, Cr, and Zn) and physic-chemical properties concentration in paint factories effluent?
- ➢ Is the concentration of heavy metals and physic-chemical in paint waste water, within the permissible limits proposed by WHO and ES?
- ➢ Is that the efficiency of the wastewater treatment plant of paint factories effective?
- ➢ What are the effects of paint factories waste water on seed germination and growth of solanum lycopersicum (tomato) and D. carota (carrot)?

1.5 Significance of the Study

The outcome of this study will be particularly important for health personnel, environmentalists, administrators and the public at large. It is believed to initiate health case study in urban settings and also urge educational psychologists to evaluate the influence of heavy metals and other chemicals on the cognitive ability of young children in towns. From literature survey, no work has been carried out on effects of paint factory waste water on seed germination and growth of solanum lycopersicum (tomato) and D. carota (carrot). So the result of this study will also serve as the basis for proposing possible methods to determine heavy metals concentrations in vegetables and initiate health case studies. Furthermore, it may motivate the Environmental Forest and Climate Change Commission, Ministry of Health, Federal Police Commission, Addis Ababa Water and Sewage Authority, and Ministry of Agriculture to conduct more dedicated and focused research in the area. Moreover, the findings could be used to compare the efficacy of some measures that would be taken to reduce the release of heavy metals to the environment.

2. LITERATURE REVIEW

2.1 Overview of paint factories wastewater

Paint is composed of pigments, solvents, resins, and various additives. (Usepa, 1993) The pigments give the paint color; solvents make it calmer to apply; resins help it dry; and additives serve as everything from plasters to ant-fungicidal agents.(Aniyikaiye et al., 2019) Paints are used for different purposes, for example to protect all sorts of buildings(house painting, boats, automobiles, planes, appliances, furniture,) (Abrha & Chen, 2017) and structures from the effects of water and sun (Berihun & Solomon, 2017a)(Crow, 2015).

Due to the pigments and other chemicals, highly polluted wastewater is generated primarily during cleaning operations of mixers, reactors, blenders, packing machines and floors.(Berihun & Solomon, 2017b). The wastewater contains appreciable concentrations of carbon (biological oxygen demand (BOD) or chemical oxygen demand (COD)), suspended solids, toxic compounds and color (Y.Njolly, 2016.) Consequently the wastes of these industries are disposed into drains, canals and rivers without treatment and the solid wastes are dumped into surrounding land or water bodies which contaminate the soil or water with highly toxic inorganic or organic pollutants.(Ayyasamy, Yasodha, et al., 2008). On close examination of manufacturing process of various paints, it is observed that water is not a constituent in any of the production processes of resins, varnishes, lacquers, etc. However, water is highly required for the manufacture of water-based paints and cooling of the ball mills or sand mills in manufacture of oil paints.

Many methods are currently used for the treatment of paint wastes in water before safe disposal. (Huang & Ghadirian, 1974) As these waters are characterized by high organic load and high suspended solids content, conventional treatment methods can be successfully applied. The most common method is the coagulation–flocculation, followed by gravity sedimentation(Bouranene & Fievet, 2015) . Less commonly applied methods are: flotation(Tian & Kong, 2012) sorption on solids,[4] as well as advanced treatment methods i.e., ozonation, membrane filtration,(Tian & Kong, 2012) electrochemical oxidation(Bashir et al., 2012) and biological treatment(Shodhganga, 2000) . Due to the differences in composition of these wastewaters, no general rules can be safely established and each particular waste should be handled properly.

Coagulation-flocculation is widely used for wastewater treatment, as it is efficient and simple to operate (Bashir et al., 2012). In addition, the process can be directly applied without being affected by the toxicity in the wastewaters. In this process, many factors can influence its efficiency, such as the type and dosage of coagulant/flocculants (Shazly et al., 2010), pH, etc. Optimization of these factors may significantly increase the process efficiency(Tian & Kong, 2012) . However, the performance of coagulation process may be poor and may result in treated wastewaters, whose characteristics do not meet effluent standards. Consequently, a further treatment is necessary. Combinations of chemical and biological methods are used usually for effective treatment of such industrial wastewaters, since it is difficult to obtain satisfactory results by using anyone of those methods alone(Shodhganga, n.d.) . Paint wastewater contains toxic compounds and was considered as inhibiting bacterial development (Usepa, 1993). Then, in addition to chemical treatment, an appropriate biological technology is required.

Water is used for washing of floors which are littered by spillage of powders, solvents, etc. when a particular batch is finished.(Aniyikaiye et al., 2019) In cases where there is vast difference in the color shade of next batch, the mills and containers, etc. have to be cleaned. This cleaning is done by xylene which is recovered and reused(Berihun & Solomon, 2017a) . Once in a while the vessels are cleaned with caustic soda(Porwal, 2015) . This cleaning constitutes the major part of the waste-water generated which is highly alkaline in nature. Other source is the cooling tower blow down (Aniyikaiye et al., 2019). In summary, it can be stated that waste-waters from the paint manufacturing industries generally tend to be alkaline, containing some oil and grease and Biochemical Oxygen Demand (BOD), Chemical Oxygen Demand (COD) and Suspended Solids (SS). The BOD and COD values give only a gross measure of organics in the wastes. Some of the organic and inorganic compounds used in the manufacturing operations are classified as toxic and hazardous(Jaishankar et al., 2014) . Chromium, copper, lead, zinc, ethyl benzene, di-(2-ethylhexyl) phthalate, tetrachlroethylene and toluene were found in high concentrations(Jolly et al., 2013) .

The discharge of such wastewater into the environment impedes light penetration, damages the quality of the receiving streams and may be toxic to treatment processes, to food chain organisms and to aquatic life (Jolly et al., 2013) . The continuous receiving of waste water especially by water bodies poses a great threat to the aquatic life. The harmful inorganic and organic substances in the effluent degrade the normal characteristics of water by reducing the oxygen level and changing the composition of existing heavy metals and other organic constituents (Dey & Islam, 2015) . As a result the usual life style of aquatic plants and animals are greatly hampered. The effects propagate through the food chain to affect human life (Yirgu, 2011) .Paints, lacquers and varnishes are among the products that have distinct effects on environment and health (Berihun & Solomon, 2017a).

2.2 Overview of physicochemical parameters

The physicochemical parameters are such as pH, temperature, turbidity, conductivity, total dissolved solids, total suspended solids, total organic carbon, biological oxygen demand, chemical oxygen demand, dissolved oxygen, total alkalinity, sulfate, nitrate, and phosphate. Physicochemical parameters are specific, discriminatory and quantitative for the above variables to be determined at the moment of sample gathering. But there are many chemicals that may be discharged from paint industry to streams and only few chemicals are selected for predictable chemical analysis and the concentrations of contaminants vary with time exit their effect for many months or weeks (Li et al., 2010). Moreover, these wastewaters present high coloration, turbidity, strong odor, and contain high loads of organic and toxic chemical substances such as surfactants, bactericides, oils, solvents, and preservative agents (Verma et al., 2012). Therefore, the release of these effluents directly into water bodies can give rise to serious ecological instability, since the presence of color blocks the passage of sunlight, thereby preventing the photosynthesis of aquatic plants, which in turn leads to the depletion of dissolved oxygen. Besides, the mere presence of toxic substances in water bodies can cause the death of several living beings (Verma et al., 2012).

2.3 Overview of impacts of paint wastewater on the environment

A paint's production facility discharges wastewater, high in organic load (Shodhganga, 2000) .

Wastewaters effluents are characterized by containing substantial organic matter, high salinity, sulfate rich and high suspended solid (Dahunsi S, et.al 2012). From time to time, due to batch processing, peak load will be discharged. The potential pollution sources are, sludge which represents a solid waste problem, Treated water could represent a water pollution problem if not complying with relevant environmental laws. Most common toxic component of paint is from VOCs. Oil-based paints generally contain more VOCs than water-based paints (Emissions, 1992). Specific literature assessing impact of effluents from paint industry on environment are rare. Few related work include Jolly et al., (2008), where the authors determined the effects of paint effluent on soil productivity and concluded that presence of certain trace elements at concentrations higher than 25 % had negative effects on seed germination, dry matter production and the yield of corn and rice.

2.3.1 Effects of Heavy Metals

Unprocessed or allegedly preserved paint industrial effluents contain variable amounts of heavy metals such as arsenic, cadmium, nickel, copper, lead, zinc, mercury and chromium, which have the potential to contaminate crops and vegetables growing under such irrigation(Hashem & Qi, 2021) . These heavy metals have a clear effect on the aquatic flora and fauna which through bio-magnification enter the food chain and finally affect human beings as well. Heavy metal pollution is an ever rising problem of our oceans, streams, lakes and rivers ((Placeholder1) Mohsen A. 2012). Heavy metals are metallic elements that have relatively high densities and or toxic (contaminated) at low concentration (Lenntech, 2004). Heavy metals are a universal collective term, which applies to the group of metals and metalloids with atomic density 5 times or higher than water (Syman and Huton, 1986; Nriagu, 1988; Hawks, 1997). Heavy metals include cadmium (Cd), copper (Cu), lead (Pb), zinc (Zn), mercury (Hg), arsenic (As), silver (Ag), chromium (Cr), iron (Fe) and platinum (Pt). Copper and zinc are critical trace elements for living organisms at low concentration (10 mg/L). The physical characteristics of heavy metals are described by Wang (2006). Heavy metals cannot be degraded easily and are very toxic even at low concentrations (1.0-10.0 mg/L). Heavy metals are dangerous because they tend to bio accumulate. Bioaccumulation means an increase in the concentration of a chemical in a biotic organism over time, associated to the chemicals concentration in the environment and ecosystem.

Many effects observed due to heavy metals exist in water. For instance, lead toxicity (Y.NJOLLY, 2018.), cadmium toxicity (Moore & Moore, 1976) zinc toxicity (Usepa, 1993) and chromium are the major heavy metal found in paint waste that affect the environment by their toxicity.(Mohammed Awole, 2015).

Lead (Pb) is commonly used in different consumer products including household decorative paints. Lead is the most important toxic heavy metal element in paint industry, ecosystem and environment. Due to its important physicochemical properties, its use can be reviewed to ancient times. Globally it is an abundantly distributed, important yet dangerous environmental chemical (Mahaffay, 1990a). Lead is regarded as highly hazardous for animals, plants and particularly for microorganisms and aquatic ecosystem. 9 Lead exists in the oxidation states Pb^{+4} and Pb^{+2}, with the divalent form being the more constant in most aquatic environments. The speciation of lead compounds in aquatic ecosystem is complex and depends upon a number of factors, principally dissolved oxygen, pH and the concentration of other inorganic and organic compounds. The concentration of lead in water ecosystems is usually restricted by its adsorption, and by the solubility of $PbCO_3$ on to particulate matter (Dojlido and Best 1993).

Cadmium is an element toxic metal and can cause serious health and environmental problems. Recently, attention has been concentrated on its availability in soil, water, dietary products, milk, herbal drugs, medicinal plants, etc. The most common sources for cadmium in soil and plants are non-ferrous smelters, phosphate fertilizers, zinc and lead mines, and combustion of fossil fuels (Davies, 1990 and Mc Bride, 1995). Cadmium is known to be toxic for living organism even if it is present in low levels (Krejpcio, 2001).

Chromium is an essential nutrient metal, necessary for metabolism of carbohydrates (Farag et al., 2015). Chromium enters the aquatic ecosystem through effluents discharged from tanneries, textiles, electroplating, metal finishing, mining, dyeing and printing industries, ceramic, photographic and pharmaceutical industries etc. (Arunkumar et al., 2000). Poor treatment of these effluents can lead to the presence of Cr (VI) in the surrounding water bodies, where it is commonly found at potentially harmful levels to fish (Li et al., 2011; Pacheco et al., 2013). In surface waters, depending on physicochemical characteristics, the most stable forms of chromium are the oxidation states trivalent Cr (III) or (Cr3+) and the hexavalent Cr (VI) or (Cr6+). Hexavalent chromium (Cr6+) is considered to be toxic (i.e. carcinogenic) because of its powerful oxidative potential and ability to cross cell membranes. Fish assimilate Cr by ingestion or by the gill uptake tract and accumulation in fish tissues, mainly liver, occurs at higher concentrations than those found in the environment (Pacheco et al., 2013). The overall toxic impact on organs like gill, kidney and liver may seriously affect the metabolic, physiologic activities and could impair the growth and behavior of fish.

Toxic zinc makes up about 75 ppm of the Earth's crust, making it the 24th most abundant element with a density of 7.14 g/cm^3. The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption. Free Zn2+ ion in solution is highly toxic to plants, invertebrates, and even fish (FAO/WHO, 2011). Zinc salts are intestinal irritants and can cause nausea, and abdominal pain (ATSDR, 2002). Prolonged exposure to high intakes of Zn results in copper deficiency and subsequent anemia (Reilly, 2002).

Generally, accumulation of heavy metals in crop plants is of great concern due to the probability of food contamination through the soil root interface. Though the heavy metal viz. Cd, Pb and Ni are not essential for plant growth, they are readily taken up and accumulated by plants in toxic levels (Mussarat & Bhatti; 2005; Qadir et al., 1999; Bhatti & Perveen, 2005). Ingestion of vegetables irrigated with waste water and grown in soils contaminated with heavy metals poses a possible risk to human health and wildlife (Otero et al., 2000; Mussarat et al., 2007; Rattan et al., 2005; Bhatti & Mussarat, 2006). Heavy metal concentration in the soil solution plays a critical role in controlling metal bioavailability to plants. Most of the studies show that the use of waste water contaminated with heavy metals for irrigation over long period of time increases the heavy metal contents of soils above safe limits Mapanda et al., 2005, Sharma et al., 2006). Ultimately, increasing the heavy metal content in soil also increases the uptake of heavy metals by plants depending upon the soil type, plant growth stages and plant species (Ismail et al., 2005, Farooq et al., 2008).

2.4 Over view of the seed tomato (Solanum lycopersicum) and carrot (D.carota) as well

Tomato (Solanum lycopersicum) is a major horticultural crop with an estimated global Production of over 120 million metric tons (F.A.O. 2007). The cultivated tomato is a member of the genus Solanum within the family Solanaceae. (Valdes and Gray, 1998). The Solanaceae, commonly known as the nightshade family, also includes other notable cultivated plants such as tobacco, chilli pepper, potato and eggplant. (Spooner et al., 2005) Tomato classification has been the subject of much discussion and the diversity of the genus has led to reassessment of earlier taxonomic treatments. Tomato was originally named Solanum lycopersicum by Linnaeus in 1753; Lycopersicon lycopersicum (L.) Karsten has also been used (Valdes and Gray, 1998). Spooner, Anderson and Jansen, 1993; Bohs and Olmstead, 1997; Olmstead and Palmer, 1997; Knapp, 2002;, 2003; Peralta et al., 2008). Vickie. Tomato (Solanum lycopersicum) is a fruit with high carotene content that reduces cancer risk and heart diseases because of its antioxidant properties (Rao and Agarwal 2000). Among carotenes in tomato, lycopene dominates but its content varies significantly depending on variety, stage of ripening, and environment(Silva & Uchida, 2000). Humans obtain 85 % of their dietary lycopene from tomato fruit and tomato-based products. Tomato is grown using chemical as well as organic fertilizers.(Ayyasamy, Banuregha, et al., 2008) The nutritional quality of conventionally and organically grown plants has been compared mainly in terms of nutrients, vitamins, and minerals (Yanar et al. 2011). Plants experience various type of environmental stresses such as salt stress (Sairam et al. 2003), heavy metal stress (Hasan et al. 2008), UV-B-radiation (Casate et al. 2002), chilling (Van Heerden and Kruger 2002) drought stress (Porcel et al. 2003). Tomato is one of the plants which are sensitive to environmental stresses including of intensive temperature, high salinity, dryness, and environmental pollution.(Machado & Serralheiro, 2017)Cultivated carrot (Daucus carota L. subsp. sativus L.) is a common vegetable with a well-known and widely distributed weedy progenitor, wild carrot or Queen Anne's lace (D. carota subsp. carota)(Rekik et al., 2017). The cultivated carrot is a member of the Apiaceae family (Umbeliferae), members of which are also some widely cultivated plants such as parsley, parsnip, dill, caraway, fennel, celery, as well as the not so widely cultivated cumin and coriander but also includes some highly toxic plants, such as hemlock(Magsar, 2015). Carrot is the most widely grown crop of the family Apiaceae (Umbelliferae), cultivated on 1.2 M hectares globally (carrot and turnip as aggregate data) (FAO, 2011) Carrot (Daucus carota), a valuable source of vitamin A due to the presence of carotene, an orange pigment and a precursor of vitamin A, is among the various classes of vegetables that are grown in different countries(Sagardoy et al., 2009). the effect of wastewater on different crops with different percentage effects and have reported crop growth inhibition when higher concentrations of the effluent was used as compared to the control (water).(Uwah, 2015) Untreated effluent had an inhibitory effect on seed germination and seedling growth through its toxic nature.(Ayyasamy, Yasodha, et al., 2008) The polluted effluent is used for irrigation to water the vegetable crops along the bank, heavy metals and anions may enter the food chain through irrigated crops, thereby exposing consumers of these vegetable crops to bioaccumulation of trace metals and anions with time.(Mosse et al., 2010)

2.4.1 Seed germination and Factors affecting seed germination

Germination success depends on water movement through the tissues surrounding the embryo(Karunyal et al., 1994). This movement is related to the water potential in the region around the seeds and the soil water potential, which promotes a gradient of potential and can restrict water uptake by seeds, interfering directly with the germination process. When the osmotic potential of the solution is more negative than that of the by cells of the embryo germination occurs (Cavalcante and Perez 1995, Carvalho and Nakagawa, 2000). (ISTA, 1999). Seed germination is a critical event in the plant life cycle(Journal & Science, 2018), because, timing of emergence from the protective seed coat is crucial for survival and reproductive success (Nelson et al., 2009). Physiologists often consider seed germination to be the period from imbibition's up to the point that embryo growth is initiated and the embryo protrudes through any covering tissues. Seed quality analysts do not consider germination to be complete until the seedling has grown sufficiently to be able to observe and evaluate the root, hypocotyls, and cotyledons (ISTA, 1999). The completion of germination depends on embryo expansion mainly due to cell elongation driven by water uptake (Bentsink, et al., 2007). During seed germination, various stored substrates are reactivated, repaired if damaged, and transformed into new building materials necessary for the initial growth of the embryo (Hadas, 2004). Potassium nitrate (KNO3) and ethanol 70 % solution is the most widely used chemicals for promoting germination. Solutions 0.1 to 0.2% KNO3 are common in routine germination testing and are recommended by the Association of Official Seed Analysts and the International Seed Testing Association for germination tests of many species (Basra, 1994).

Tomato seeds typically germinate in 5 to 10 days if given optimal conditions(Kumari et al., 2013). You'll know seeds have germinated as soon as you see green plant emerging from the growing medium(Jolly et al., 2013). That's a time to celebrate. The production of healthy and vigorous tomato seedling is the most important factor in successful production and yield of tomato fruits. Germination of the seed is a critical stage, because the rest of the plant life is directly dependent upon the rate of its germination (Qadir and Shahzadi, 1969). Growth medium is known to have an effect on value of potted ornamental plants and plays an important role in germination rate, and many other physiological parameters including plant height, number of leaves, spike length, number of florets per spike, spike diameter and yield, etc. (Vendrame et al., 2005).

Carrot seeds will take 6 to 10 days to germinate under ideal conditions, including: temperature at 65 to 85 degrees Fahrenheit (18 to 29 degrees Celsius) (Pereira et al., 2008) (Chhabra, 2018). Soil that is moist but not soggy (do not allow the seeds to dry out or sit in too much water!) Soil that gets proper aeration (do not compact the soil!) Seeds that are healthy and new (old seeds have a lower germination rate)(Pereira et al., 2008)

Seed germination involves a number of complex cell activities, and both genetic and environmental factors and storage behavior play a key role in modifying tree seed germination (Mog"omba et al., 2007). That is, germination process is controlled by several biological (such as species, seed viability, seed dormancy, and seed size) and environmental (such as moisture availability, temperature, relative humidity, light intensity and duration) factors (Nelson et al., 2009; ISTA, 1999). High temperatures (35 - 40°C) for example, can delay or inhibit carrot seed germination and compromise the stand establishment in the field (Carneiro & Guedes, 1992;

Cantliffe & Elballa, 1994; Pereira & Nascimento, 2002; Pereira et al., 2007; Nascimento & Pereira, 2007).

2.4.2 Seedling Growth and Measurement Techniques

Growth in plants is defined as an irreversible increase in volume. The largest component of plant growth is cell expansion driven by turgor pressure. During this processes, cells increase in volume and become highly vacuolated (Taiz and Zeiger, 2002). Seedling growth is affected by conditions both above ground humidity, carbon dioxide, temperature and light as well as below ground water and mineral nutrients. Other organisms, either beneficial or harmful, can also influence plant growth (Jaenicke, 1999). Healthy seedlings need good soil and it should be well drained with a mix of sandy and loamy soil, high in humus and nutrients and slightly acidic (Moir et al., 2007). The site preparations with the humus layer increase seedling nitrogen uptake. Moreover, seedling nitrogen uptake was correlated to root growth (Nordborg, 2001). The seedling growth in height, root collar diameter, number of leaves, tap root length and number of primary roots distinctly varied with biomass allocation indicated by the root to shoot ratio. But the growth of root is determined by the physical force of the soil which is highly dependent on both soil moisture and bulk density (Daddow and Warrington, 1983). The bulk density of the soil is in turn determined by the texture of the soil. Measurements of above-ground biomass could be made through two basic ways: destructive and non-destructive methods. Among the various methods for evaluating forest biomass, the most widely used is the destructive method. However, the methods are not suited to natural environment, especially if the environment is highly degraded and also with threatened species (Montes et al., 2000). In addition, this method is expensive in terms of time and expended for collecting the data when compared with the non-destructive method. The other alternative way of measurement of biomass is non-destructive method. Because total harvesting is impractical in forest studies; other methods have been developed to estimate total biomass from non-destructive measurements such as recording the height of selected plants (Vann et al., 1998). The non-destructive measurement technique has the following advantages: 1) it enables to study evolution of individual tree biomass and its components by taking photographs at several year intervals (Montes et al., 2000); 2) it can determine the biomass and leaf area of individual trees throughout their growing cycle without disturbing the environment (Montes et al., 2000; Vann et al., 1998)

2.5 Paint waste water Environmental Standards for Industrial Pollution Control

Table 2. 1 Paint waste water discharge standard

Standards	PO_4^{3-} (mg/l)	NO_3^- (mg/l)	SO_4^{2+} (mg/l)	pH	TDS (mg/l)	EC (mS/m)	COD (mg/l)	BOD (mg/l)	Cr^{+6} (mg/l)	Zn^{+2} (mg/l)	Cd (mg/l)	Pb (mg/l)	Reference
ES	10	-	-	5.5 – 9.5	3000	-	-	-	0.1	1	0.2	0.5	(Berihun & Solomon, 2017b)
WHO	15	45	300	6 – 9	1500	150	120	60	0.05	0.2	0.01	0.01	(Aniyikaiye et al., 2019) (WHO,2006)

*EC = Electrical Conductivity, *TDS = Total dissolved solids,, BOD= Biochemical oxygen demand, COD= Chemical oxygen demand

2.5.1 Industrial waste water and Irrigation Water Quality Standards

Water from these sources contains substantial amount of needless or unwanted substances dissolved in water that may deteriorate soil fertility and crop growth and crop yield. These unwanted substances have come from manmade or natural (domestic and industrial effluents) sources and their harshness depends upon the type of particulate and its quantity which resulted in deteriorated water quality.

The following are the main characteristics to assess the quality of irrigation water.

- Electrical Conductivity (EC)
- Residual Sodium Carbonate (RSC)
- Total Dissolved Solids (TDS)
- Sodium Adsorption Ratio (SAR)

There are numerous water quality standards by different organizations. The US Regional Salinity Laboratory and Food and Agriculture Organization (FAO) have given the quality of irrigation water as shown in table 2.2

Water Quality Classification	EC at 25 °C (mS/m)	TDS (mg/L)	SAR (meq/L)	RSC (meq/L)
Excellent	<250	500-1500	Up to 10	<1.25
Good	<160	2250-4000	10-18	1.25-2.5
Medium	250-750	1500-2500	18-26	>2.5
Bad	160-500	>4000	>26	-
Very Bad	750-2250	>2500	>26	-

Table 2.2 Irrigation Water Quality Standards (US Regional Salinity Laboratory and FAO) (Chhabra, 2018)

3. METHODOLOGY

3.1 Study area

This study was carried out in the sub-city of Gelan, Oromia Region, 37 kilometers southeast of Addis Ababa and 10 kilometers northwest of Bishoftu, and Addis Ababa, Ethiopia. Gelan's geographical coordinates are 8° 52' 0'' North, 37° 47' 0'' East with an elevation of 1950 meters above sea level. Addis Ababa (9°N, 38.5° E) is the capital city of the Federal Democratic Republic of Ethiopia situated in the high plateaus of central Ethiopia in the North- South oriented mountain system neighboring the rift- valley. The city, established in 1896, has experienced several planning changes that have influenced its physical and social growth. Addis Ababa is situated at 1500-3100 meters above sea level with a total land area of 54,000 hectares and an aggregate population density of 4,848 persons per square kilometer. For administrational purposes, the city is divided into 11 sub-cities. It is also home for the African Union, the Economic Commission for Africa and other international organizations. The city plays a significant role in the economic, social and political development of the country. A preliminary visit in the study area was undertaken in order to select sampling sites. The selection of these sampling sites were based on the location (residential and commercial) by considering the relative amount of paint effluent wastewater discharging factories at the sites in both Gelan and Addis Ababa. Primary data were obtained from the three selected sites. Cadisco Paint, Zemilli Paint, and Nifas Silk Paint factory. Waste water sampling was made on site by applying stratified random sampling technique.

3.2 Sample collection

The paint wastewater effluent samples were collected randomly three times in a year from three different paint factories. Polythene bottles of 2.5 L and 2 L were used to collect the waste water samples. Sampling bottles were washed 3-4 times with waste water from the exact site of sampling prior to collection of the waste water samples. The waste water samples used for COD and BOD determinations were collected directly into BOD bottles and some drops of manganese sulfate solutions were added to fix dissolved oxygen (JingxiMa et al, 2020). The entire samples container were appropriately labeled, identified and distinguished from each other for further separation in the laboratory. Then after, the labeled samples waste water were transported for six consecutive days to Addis Ababa University ,Chemistry Department laboratory and the Centre of

Environmental Science so that appropriate sample receipt, storage, analysis and arrangements were provided and stored in the refrigerator at about 4°C prior to analysis.

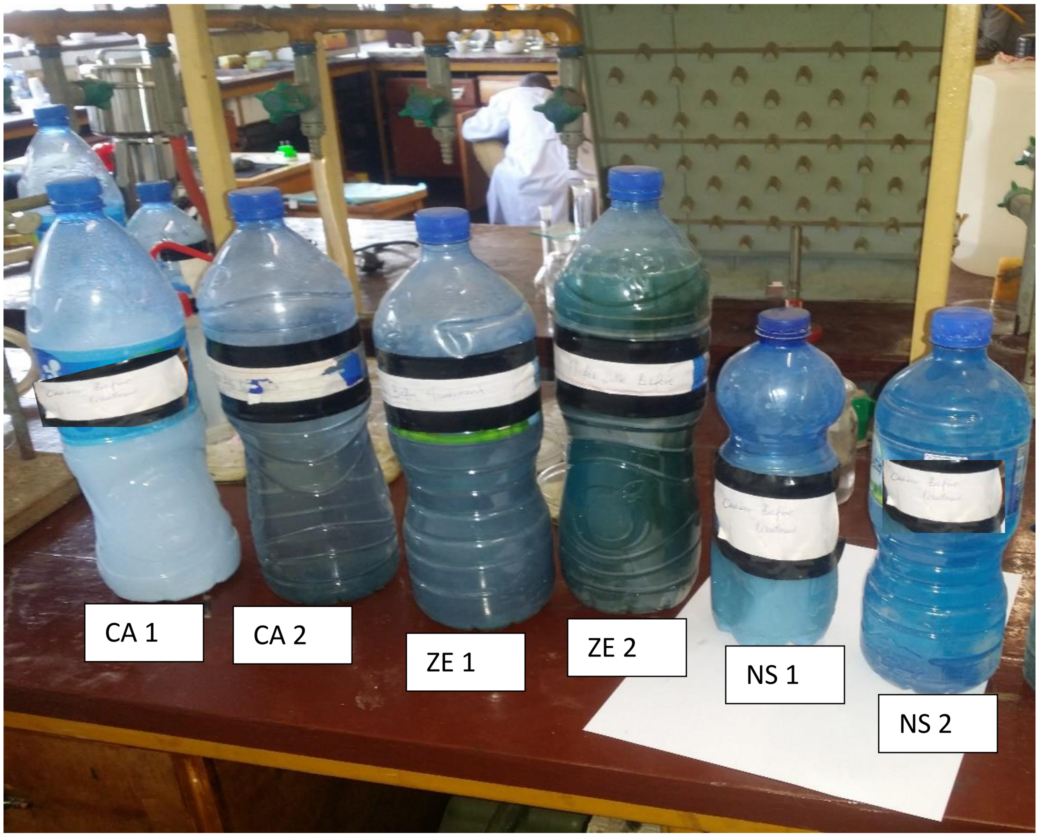

Figure 3.1 Samples collected from different paint factories

3.3 Apparatus and Instruments

The following apparatus and instruments were used in the project work. Polyethylene bottles, micro pipettes, vials, pipettes , beakers, volumetric flasks, different size measuring cylinders, funnels, graduating cylinders, thermometers, Whatman filter papers No.42, refrigerators, hot plates, Flame AAS (ZEEnit 700 P Spectrometer(Analytikjena) (Eser et al., 2004) petri-dishes, oven, spray, ruler, electronic beam balance, spatula and a pair of scissors.

3.4 Sampling Analysis

3.4.1 Physicochemical analysis

All field meters and equipment were checked and calibrated according to the manufacturer's specifications. Analytical tests of the collected water samples were performed for various parameters such as pH, turbidity, chemical oxygen demand (COD), biological oxygen demand

(BOD), conductivity (EC), total dissolved solids (TDS), ammonia, sulfate, nitrate, and phosphate. All the tests were conducted at the laboratories of Addis Ababa University, Chemistry Department, and Environmental Science Department and at the Ethiopian Federal Basin Development Authority. Parameters such as total dissolved solids (TDS), biochemical oxygen demand, sulfate, nitrate, and phosphate were analyzed using the standard analytical methods as described by APHA (Sinha, 2011). pH was determined by potentiometric method. Biological oxygen demand (BOD) was measured based on oxygen consumed in a 5-d test period (5-d BOD or BOD_5) at 20 °C after arrival of the samples at the laboratory (O. Eur, 2008). Electrical conductivity (EC) of water samples were measured by digital conductivity meter. Total dissolved solids (TDS) determined using gravimetric method. Ammonium (by stannous chloride method), nitrate, and phosphate of the wastewater sample were measured by Uv-Vis spectrophotometer. The chemical oxygen demand is the measurement of the amount of oxygen in water and wastewater consumed for chemical oxidation of pollutant. COD values were measured by Hach Lange kits using HACH DR/2800 spectrophotometer.

3.4.2 Heavy Metal Determination (Cd, Pb, Zn, and Cr)

The paint factory wastewater samples were digested as follows: The sample, 100cm³ was transferred into a beaker and 5ml concentrated HNO_3 was added (Usepa, 1992) . The beaker with the content was placed on a hot plate and evaporated down to about 20 ml(NAND SINGH et al., 2012) . The beaker was cooled and another 5ml concentrated HNO_3 was also added. The beaker was covered with watch glass and returned to the hot plate. The heating was continued, and then small portion of HNO_3 was added until the solution appeared light colored and clear. The beaker wall and watch glass were washed with distilled water and the sample was filtered to remove any insoluble materials that could clog the atomizer. The volume was adjusted to 100cm³ with distilled water(Nand Singh et al., 2012) (El-Nahhal et al., 2013). Through acid digestion of the samples, followed by Flame Atomic Absorption Spectrometry, as recognized by the WHO as appropriate for the purpose. Calibration curves were plotted for each of the metals separately, by running various concentrations of standard solutions at specified wavelengths. Atomic Absorption Spectrophotometer (Model ZEENIT 700P) was used to determine the metal concentrations in the water sample. Instrument calibration was done using the standards before determination of the sample. A reagent blank sample was also analyzed. The concentration of the metal was obtained from the difference between the readings of the samples and that of the blank (Skoog et al., 2005).

3.5 Seed collection, germination and growth experimental analysis

Seeds (Solanum lycopersicum (tomato) and D. carota (carrot)) vegetables (Harvest General Trading) were collected in plastic petri dishes and stored in the laboratory for seed germination and growth. Tomato plants that have been well nourished by organic matter are said to produce healthy fruits with higher dry matter content, flavonoid, and ascorbic acid content compared to fruit from conventional production (Premuzic et al., 1998; Stertz et al., 2005; Mitchell et al., 2007). Carrot is a root vegetable with carotenoids, flavonoids, polyacetylenes, vitamins, and minerals, all of which possess numerous nutritional and health benefits The major vegetable crop grown around Upper Awash tributaries are lettuce, Swiss Chard, carrot, kale, cabbage, potato, zikuni (cucumber), cauliflower, beans, tomato, pepper and onion. The communities, who live around Akaki River and in Addis Ababa city consume carrot and tomato vegetables (Y & M, 2018)

Figure 3.2 The Seeds collected from Harvest General Trading

The experiments were conducted at Addis Ababa university, chemistry department laboratory and all petri plates prepared with double layers of filter paper (Whatman No. 2) (Uzma et al., 2016). Three replicates of the sterilized petri dishes for each dilution lined with blotter paper were arranged for the study. Before using, all glassware were autoclaved at 121 °C for 15 min (Kaydan & Yagmur, 2008). Seeds were disinfected by soaking in 70 % ethanol for 5 min and then rinsed with distilled water. Two different concentrations (50% and 100 %) and a control were tested for both wastewater samples with each vegetable seed. Ten seeds were kept in each petri dish. The control plates were treated with deionized water. All experiments were conducted in three independent replicates. At the beginning of the experiments, filter papers were moistened with 5 ml of the respective concentration of wastewater. Later on, 2 ml of the respective solution was added after every 48 h (Sevik, 2016). All petri plates were randomly placed on the table at 23 °C(Taylor et al., 2000.). This is calculated by the number of seedlings germinated to the total number of seedling sown in each set of petri dish.

$$GP \quad = \frac{Ng}{Ns} * 100$$

All the germination and early seeding growth parameters were evaluated using the method used by (Almodares et al., 2007b) by counting germinating seeds starting after 24 hours of sowing every day for 7 days. A seed was considered to be germinated when the radicle emerged up to 2 mm. The length of root and shoot was measured with a measuring tape after separating the seedlings into roots and shoot (Özkara et al., 2011). The root length, shoot length of the germinated seed was measured in cm scale using a ruler (Samadi, 2014).

3.6 Data presentation and analysis

Variations of each parameter between sites were analyzed using one way analysis of variance (ANOVA). Data points in the tables and figures represent the means, with all error bars shown (±1 standard error of mean). Both the mean and standard deviation were performed where appropriate using the statistical package on Microsoft Excel Version 2016. The level of significance used for all statistical tests is 5% ($p<0.05$). WHO irrigation water quality standard was used for the selection of the paint waste water for seed germination and growth (Aniyikaiye et al., 2019) .

The reduction efficiencies of the various parameters were calculated by equation below:

$$\text{Reduction efficiency} = \frac{\text{Concentration in the influent - Concentration in the effluent}}{\text{Concentration in the influent}} * 100\%$$

4. RESULTS AND DISCUSSION

The laboratory results of investigation of three paint factories' effluents for various determination of heavy metals and physicochemical parameters are presented in Table 4.1

Table 4.1 Trace metal and physicochemical parameters analyses results

All values are expressed in mg/L, except pH and EC

Code	**PO_4^{3-}**	**NO_3^-**	**SO_4^{2+}**	**NH_3**	**NH_4^+**	**pH**	**TDS**	**EC**	**COD**	**BOD**	**Cr^{+6}**	**Zn^{+2}**	**Cd**	**Pb**
CA 1	34.20	20.73	1440.00	36.30	38.70	9.00	316.00	656.00	653.67	151.62	BDL	1.00	BDL	1.02
CA2	1.47	12.50	140.00	0.33	0.35	7.80	410.00	858.00	283.00	6.40	BDL	0.02	BDL	0.06
NS1	5.19	2.85	498.00	2.85	3.17	8.05	381.00	790.00	534.67	179.33	BDL	1.03	BDL	1.09
NS2	1.31	0.68	188.33	0.43	0.46	8.50	1270.00	2540.00	322.67	35.76	BDL	0.01	BDL	0.01
ZE 1	19.72	17.06	1242.67	7.50	8.10	6.80	453.00	940.00	720.00	275.36	BDL	1.05	BDL	1.05
ZE 2	1.52	0.77	32.33	0.39	0.42	7.80	805.00	1637.00	485.00	35.42	BDL	0.02	BDL	0.06

Standard effluent discharge limit values are presented in Appendix 3. Laboratory results of trace metal and physicochemical parameters' values comparison with the standard limits values (WHO) were undertaken by graphical analysis and using MS Excel.

4.1 pH

The observed pH values in some of the paint factories effluents are shown in Table 4.1. The pH of wastewater during treatment is essential for the removal of organic compounds and heavy metals. Alkaline pH favors the precipitation of most metals as insoluble solids (Permenkes, 2018). The extremely low pH of effluent is generally not acceptable, as low pH cause problems to survival of aquatic life. The range of the measured pH values from CA, NS and ZE were 7.8, 8.5, 7.8, respectively, indicating the alkaline nature of the paint effluent. The vessels used in manufacturing processes have to be cleaned before change of product.. Thus, the waste-water pH is in range of 8.5 to 13.5. At high pH, most of the metals become insoluble and accumulate in the sludge and sediments. The toxicity of heavy metals also gets enhanced at particular pH. However, entire pH values lie within the guideline limits of WHO and ES permissible range of 6–9 and 5.5 – 9.5, respectively(Industries, 2019)(World Health Organization, 2006).

4.2 COD (Chemical Oxygen Demand)

The chemical oxygen demand (COD) is the estimate of oxygen essential for the portion of organic matter in wastewater that is subjected to oxidation and also the amount of oxygen consumed by organic matter from boiling acid potassium dichromate solution.(Nand Singh et al., 2012)(Regime, 2015), While biological oxygen demand (BOD) is a measure of the amount of oxygen required to remove waste organic matter from water in the process of decomposition by aerobic bacteria (those bacteria that live only in an environment containing oxygen)(Ilyas et al., 2019). BOD and COD indicate the pollution of water by oxygen depletion(Samudro & Mangkoedihardjo, 2010). The COD value is usually higher than the BOD, because some organic materials in the water that are resistant to microbial oxidation and hence not involved in BOD could be easily chemically oxidized. COD measurements can be made in a few hours, while BOD measurements usually take five days (BOD_5)(Aslam, 2010). The COD of the influent wastewater generated from paint factories CA, NS and ZE were 653.67mg/l, 534.67mg/l, and 720.00 mg/l, respectively. Results obtained after treatment gave 56.71%, 39.65%, and 32.63% reduction efficiencies in COD levels of WWTPs used in the aforementioned sites. (Figure 4.1). The presence of oxidizable inorganic compounds such as extenders, pigments and additives were accountable for the high concentration of chemical oxygen demand in the samples. The maximum COD value of 485 mg/l was found in ZE and the lowest value 283 mg/l was observed in CA. the values of COD from all paint factories under consideration did not comply with set limit value both ES (250 mg/l) and

WHO standards (120 mg/l) (World Health Organization, 2006). The most common application of COD is in measuring the amount of oxidizable contaminants (pollutants) found in surface water (e.g., lakes and rivers) or wastewater (Walakira & Okot-Okumu, 2011).

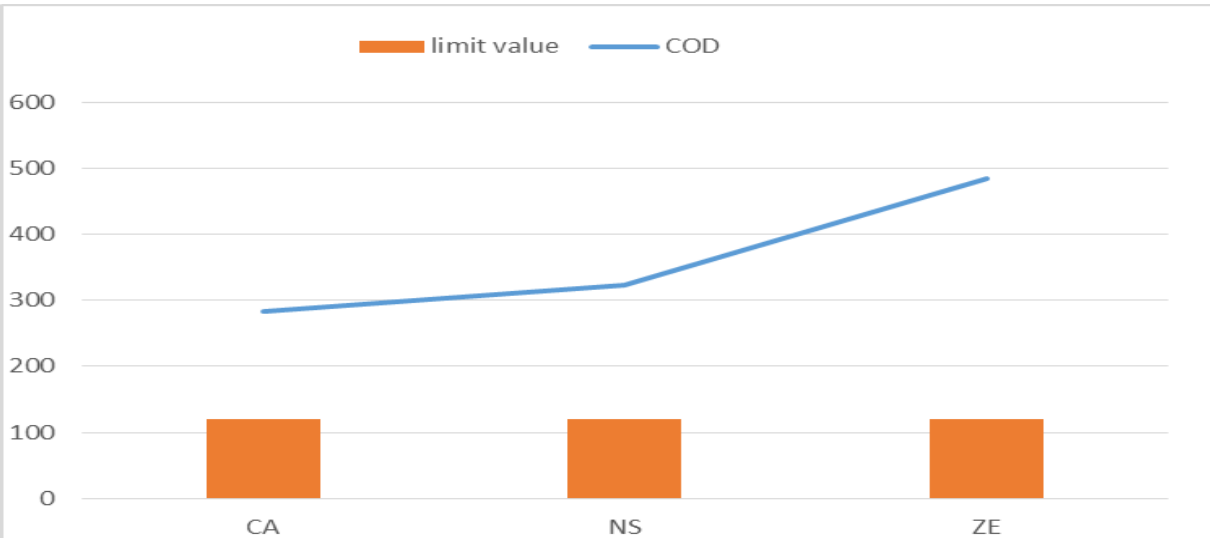

Figure 4.1 Comparison between effluent of COD and paint effluent discharge limit value.

4.3 BOD (Biological Oxygen Demand)

Biological oxygen demand is an important parameter for usage conditions of surface waters. It is an approximate measure of the amount of biochemical degradable organic matter present in a water sample. It is defined by the amount of oxygen required for the aerobic microorganisms present in the sample to oxidize the organic matter to a stable organic form (Yirgu, 2011)(Chapman, 1992). The higher the BOD concentration, the greater the extent of oxygen depletion in the water bodies. This results in the reduction of oxygen available for higher forms of aquatic life, which consequently leads to the death of aquatic organisms (Mojid et al., 2019). The BOD of the influent wastewater generated from paint factories CA, NS and ZE are 151.62 mg/l, 179.33 mg/l, and 275.36 mg/l, respectively. Results obtained after treatment gave 95.78% 35.76% and 35.42% reduction efficiencies in BOD levels of WWTPs used in these paint factories (Figure 4.2).The effluents from all the selected paint factories with BOD values of 6.40 mg/l, 35.76 mg/l , and 35.42 mg/l comply with WHO (60 mg/L) BOD standard (World Health Organization, 2006). However, high BOD level in the effluent could be attributed to the availability of organic compounds such as pure acrylic and styrene acrylic binders, cellulose thickener and organic pigments, which could be broken down by micro-organisms(Y.Jolly.et.al,2020).

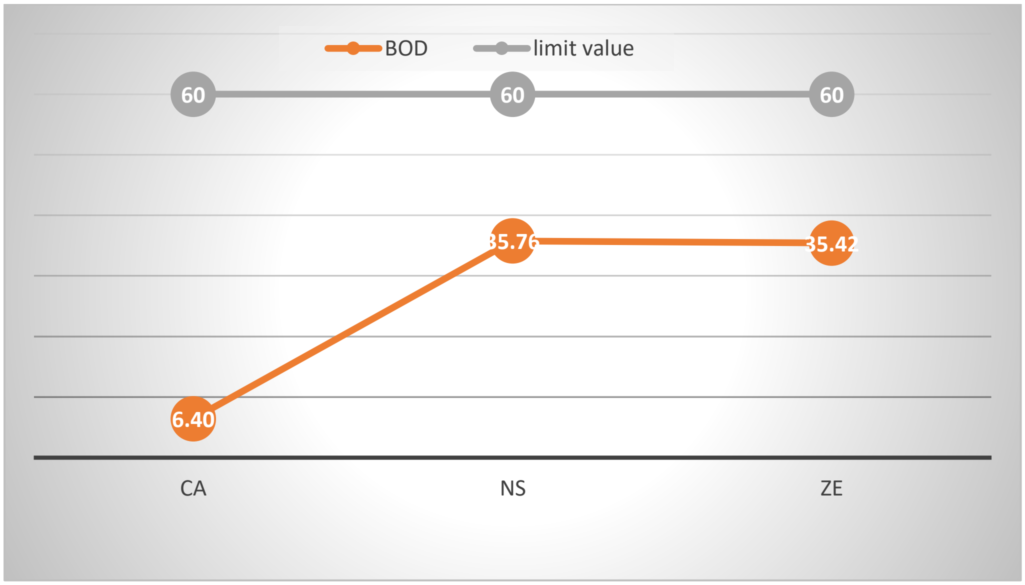

Figure 4.2 Comparison between effluent of BOD and paint effluent discharge limit value

4.4 Sulfate, Nitrate, and Phosphate

When nitrate and phosphate ions concentrations in shallow water bodies are in excess, there is overgrowth of water plants leading to the formation of algal bloom. This causes a high consumption of dissolved oxygen in water (Permenkes, 2018). Sulfate is an essential nutrient for tissue growth in plants and animals(Ma et al., 2020). The reduction oxidation ability of sulfates via chemical and microbiological pathways makes them an important link in the global sulfur cycle. On treatment, the obtained sulfate reduction efficiencies were 90.28 %, 62.18% and 97.39% for CA, NS and ZE, respectively. Treatment of raw wastewater from NS resulted in an high concentration of sulfate (188.33 mg/L) and complies with set limit value based on the WHO guideline value of 300 mg/ L. (World Health Organization, 2016).

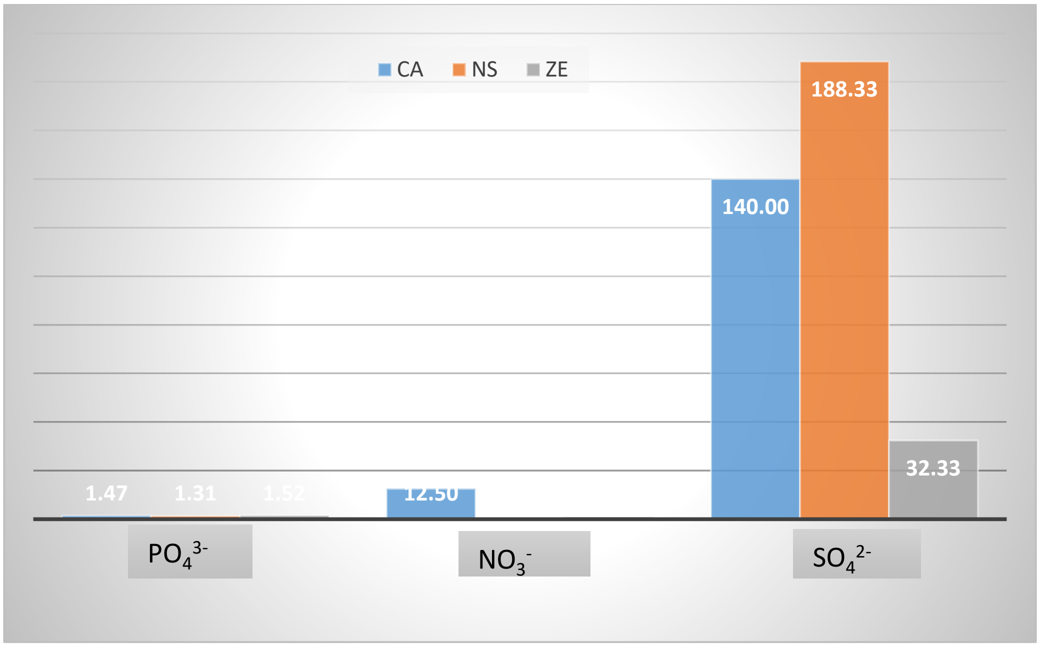

Figure 4.3 the status of phosphate, sulfate and nitrate concentration in different paint factories effluents

The effluent treatments used in all the examined paint factories were efficient in the reduction of sulfate. Nitrate is an essential nutrient for many photosynthetic autotrophs and in some instances, functions as a growth-limiting nutrient. It is used by algae and other aquatic plants to form plant protein, which in turn, can be used by animals to form animal protein. Nitrate is a major ingredient of farm fertilizers and is necessary for plant uptake and is essential for plant growth.(Gassama et al., 2015). Nitrates are the indirect source of food for fish. This may increase the fish population. However, if algae grow too wildly, oxygen levels will be reduced and fish will die. Results obtained after treatment gave 39.70% 76.14 % and 95.48% reduction efficiencies in nitrate levels of WWTPs used in paint factory of CA, NS and ZE. Respectively (Figure 4.3). The nitrate of the influent wastewater generated from paint factories CA, NS and ZE were 12.50 mg/l, 0.68 mg/l and 0.77 mg/l, respectively. Treatment of raw wastewater from CA resulted in a high concentration of nitrate (12.50 mg/l). The levels of nitrate in all the sampling points are lower than the WHO limit of 45 mg/L(World Health Organization, 2016). Increase in nitrate, like increase in any salt will increase the osmotic concentration of the soil solution. The roots of the plants then have to take up minerals from a more and more concentrated solution. If the solution outside gets too concentrated, there will come a point where the plant is not able to take up any water against the concentration gradient and the plant will start to wilt. Even before this point is reached, the plant will grow slowly (Divya et al., 2015)(John H. 2021).

Phosphorus is essential for all living beings and it also serves as an important macro-nutrient for biological tissues(Silva & Uchida, 2000). The experimental results revealed that, among three paint factories, the maximum concentration of phosphors was observed in ZE (1.52 mg/l) and the lowest observed value of 1.31 mg/l was found in CA paint factory (Table 4.1) and Figure 4.3. However almost the three factories have related values. The observed values ranged between 1.31 – 1.52 mg/l. Results obtained after treatment gave 95.71%, 74.82%, and 92.29% reduction efficiencies in phosphorus levels of WWTPs used in paint factory of CA, NS and ZE, respectively (Figure 4.3). Phosphors concentration of the three paint factories were found within the limit value of ES and WHO guideline (10 mg/l and 15mg/l), respectively. (Aniyikaiye et al., 2019)((Berihun & Solomon, 2017b). The element phosphorus is necessary for plant and animal growth. Nearly all fertilizers contain phosphates. Phosphates enhance the growth of plankton and water plants that serve as food for fish and aquatic life which results in increase of fish population that improves the quality of aquatic life. If excess phosphate is present, it may result in eutrophication. Many fish and aquatic organisms may not survive.(Ma et al., 2020).

4.5 Total Dissolved Solids (TDS)

Total dissolved solids is a measure of all dissolved substances in water(Aniyikaiye et al., 2019). In other words, TDS is a measure of inorganic salts, organic matter and other dissolved materials in water. The waste water with high TDS value may cause salinity problem if discharged to irrigation water.(Abrha & Chen, 2017). In this study, experimental data showed that TDS of paint effluent increase from raw waste water to treated waste water. Thus, CA 316.00 to 410.00 mg/l, NS 381.00 to 1270.00 mg/l, ZE 453.00 to 805.00 mg/l and this increase could be as a result of the presence of dissolved ions of resins, organic and inorganic solvents and additives like surfactants, coalescing and anti-cracking agent found in paint as well as the dissolved ions of the chemical reagents used for the effluent treatment in these paint companies. The experimental results revealed that, among three paint factories, the maximum concentration of TDS was observed in NS (1270 mg/l) and the lowest observed value of 410 mg/l was found in CA paint factory. All the values of TDS fall within permissible limits limit of 500 mg/l for discharge into potable waters (Figure 4.4). High concentration of TDS can result in dehydration of aquatic animals (Aniyikaiye et al., 2019).

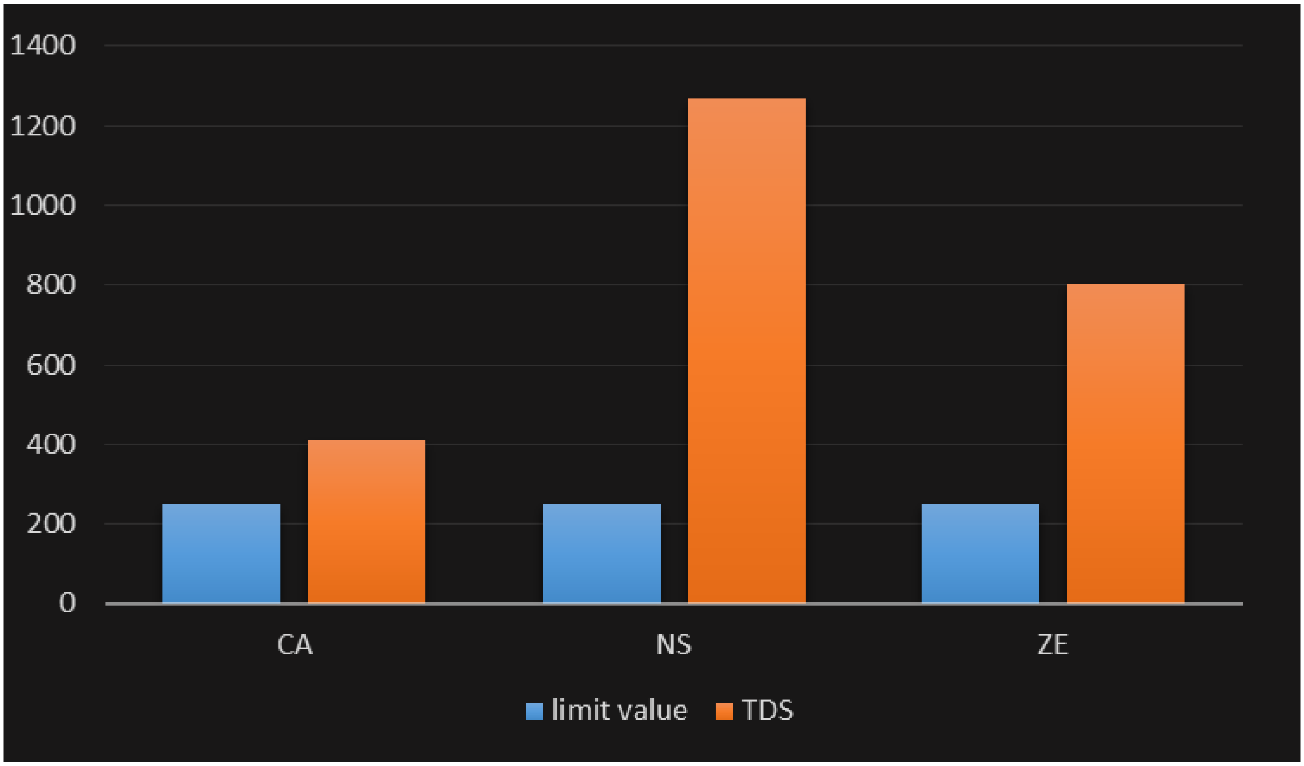

Figure 4.4 Comparison between effluent TDS and paint effluent discharge limit value.

4.6 EC (Electrical Conductivity)

Conductivity is a measure of water's capability to pass electrical flow. This ability is directly related to the concentration of ions in the water and it is dependent on water temperature and salinity/TDS(Ma et al., 2020). Inorganic ions have major influence on the conductivity of water. High values of EC show that inorganic ions are in abundance in the wastewater. The conductivity of the water is one of the important parameters used to determine the suitability of water for irrigation.(Chhabra, 2018) It is a useful indicator for salinity or total salt content of waste water. Treatment of wastewater from the three selected paint industries resulted in increase in EC from 656.00 to 858.00 mS/m 790.00 to 2540.00 mS/m, 940.00 to 1637.00 mS/m for CA, NS and ZE, respectively. The effluents from all the selected companies with EC values do not comply with WHO (Aniyikaiye et al., 2019)(60 mg/L) EC standards.(Figure.4.5) High EC values can result in a physiological drought which restricts root water uptake by the plant, even when the substrate is moist (El-Nahhal et al., 2013).

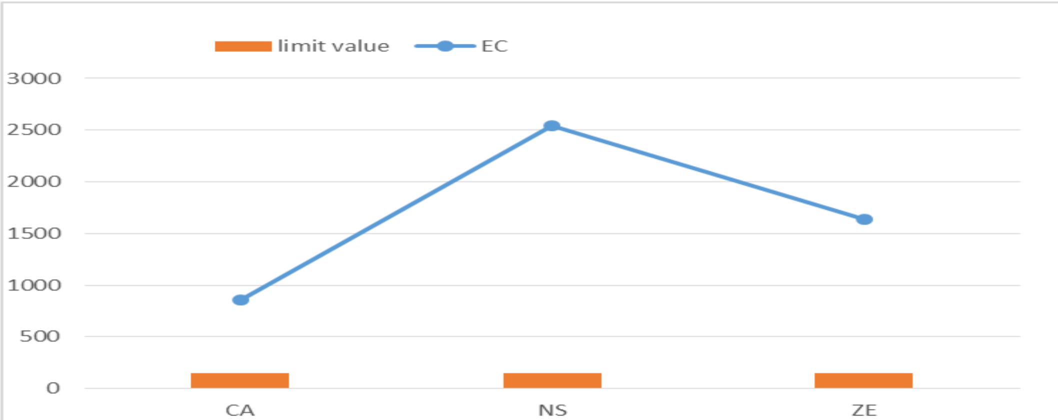

Figure 4.5 Comparison between effluent of EC and paint effluent discharge limit value.

4.7 Lead (Pb)

Lead is the most important toxic heavy metal element in paint industry, ecosystem and environment. (Wani et al., 2015) Due to its important physicochemical properties, its use can be dated to ancient times. Globally it is an abundantly distributed, important yet dangerous environmental chemical (Mahaffey, 2017). In the present investigation, it was observed that the maximum concentration of Pb was 0.06 mg/l in effluent samples collected from CA and ZE paint manufacturing factories. In many plants, 90% of the total Pb is accumulated in their roots. Most Pb in roots is localized in the insoluble fraction of cell walls and nuclei, which is linked with the detoxification mechanism (Fahr et al., 2013). On treatment, the obtained lead reduction efficiencies were 50%, 88.88% and 60 % for CA, NS and ZE, respectively. Besides, the minimum concentration of Pb (0.01 mg/l) was found in the effluent samples collected from NS paint factories that meet Ethiopian Standard (ES) (0.5mg/l) and WHO (0.01 mg/l). (Figure.4.6) However, the two paint factories, Cadisco and Zemilli do not comply with the above standards. (World Health Organization, 2016). Lead toxicity may be caused through fruits and vegetables contaminated with high lead levels from the soils where they are grown(Wani et al., 2015).

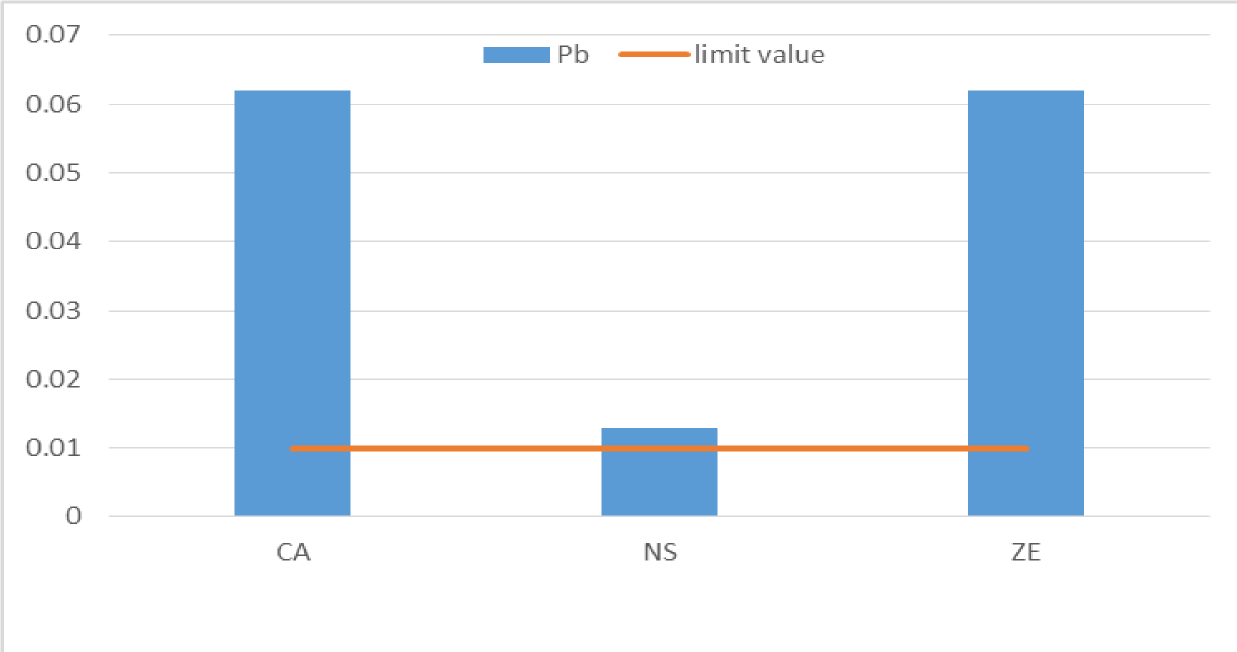

Figure 4.6 Comparison between effluent of trace metal Pb and paint effluent discharge limit value

4.8 Zinc (Zn)

The toxicity of Zn is as a result of excessive absorption which suppresses copper and iron absorption. While free Zn^{2+} ion in solution is highly toxic to plants, invertebrates, and even fish (Amdie, 2018). The concentration of Zn was recorded (0.02 mg/l maximum) in waste water effluent samples collected from Kadisco and Zemilli paint manufacturing sites, while minimum means concentration of 0.01 mg/L was found in effluents collected from Nifas Silk (NS) paint factories. On treatment, the obtained Zinc (Zn) reduction efficiencies were 98% 99.03% and 98.09 % for companies CA, NS and ZE, respectively. The results of the present investigation indicate that concentration of Zn in different industrial effluent samples sites was below the permissible limit of 1 mg/l ad 0.2 mg/L as per ES and WHO standards reported that the range of values for zinc concentration in all the sampling points was between 0.01-0.02 mg/l (Figure 4.7). Zn plays a biochemical role in the life processes of all aquatic plants and animals; therefore, it is essential in the aquatic environment in trace amounts. Zinc is used in a number of alloys including brass and bronze, batteries, fungicides, and pigments. Zinc is an essential growth element for plants and animals, but at elevated levels, it is toxic to some species of aquatic life (Ma et al., 2020).

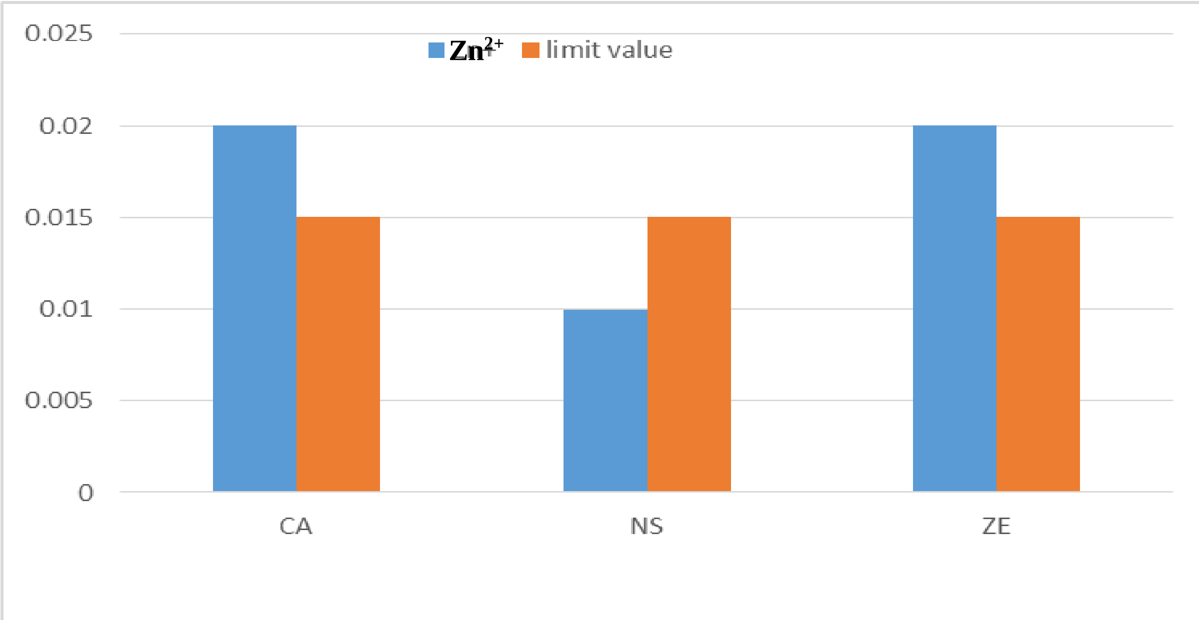

Figure 4.7 Comparison between effluent of trace metal Zn^{2+} and paint effluent discharge limit value

4.9 Cadmium (Cd)

Cd is contributed to the surface water through paints, pigments, glass enamel, and deterioration of the galvanized pipes etc. The major route of cadmium exposure for the general population is via food. An increase in soil cadmium content generally results in an increase of plant uptake of cadmium although some soil and plant factors may influence cadmium accumulation by plants. Crops grown in cadmium contaminated areas have been found to contain elevated cadmium content compared with normal levels. Therefore, human cadmium exposure via food in contaminated areas can be many times above normal intakes and lead to cadmium toxicity. The concentration of cadmium in both the raw and treated effluent from all the examined sites were below the detection limit (Table 4.1).

4.10 Chromium (Cr)

Chromium is generally more toxic at higher temperatures and its compounds are known to cause cancer in humans. Chromium-containing inorganic pigments are used in paint manufacture, hence the presence of chromium in the effluents (Costa, 1997). High concentrations of chromium exhibited severe necrosis and a host of other growth abnormalities and anatomical disorders (Aniyikaiye et al., 2019). The experimental data showed that the Cr concentration in wastewater samples was detected at all sites (Table4.1). The concentration of chromium in both the raw and treated effluent from all the examined sites were below the detection limit (Table 4.1).

4.11 Effect of paint wastewater on germination

The effect of CA paint industry wastewater on seed germination of the solanum lycopersicum (tomato) and D. carota (carrot) vegetables is shown in Figures 4.8-4.11.

In solanum lycopersicum (tomato), germination started 48 h after sowing. The effect of paint industry wastewater on the germination was dependent on the concentration of wastewater and duration of exposure.

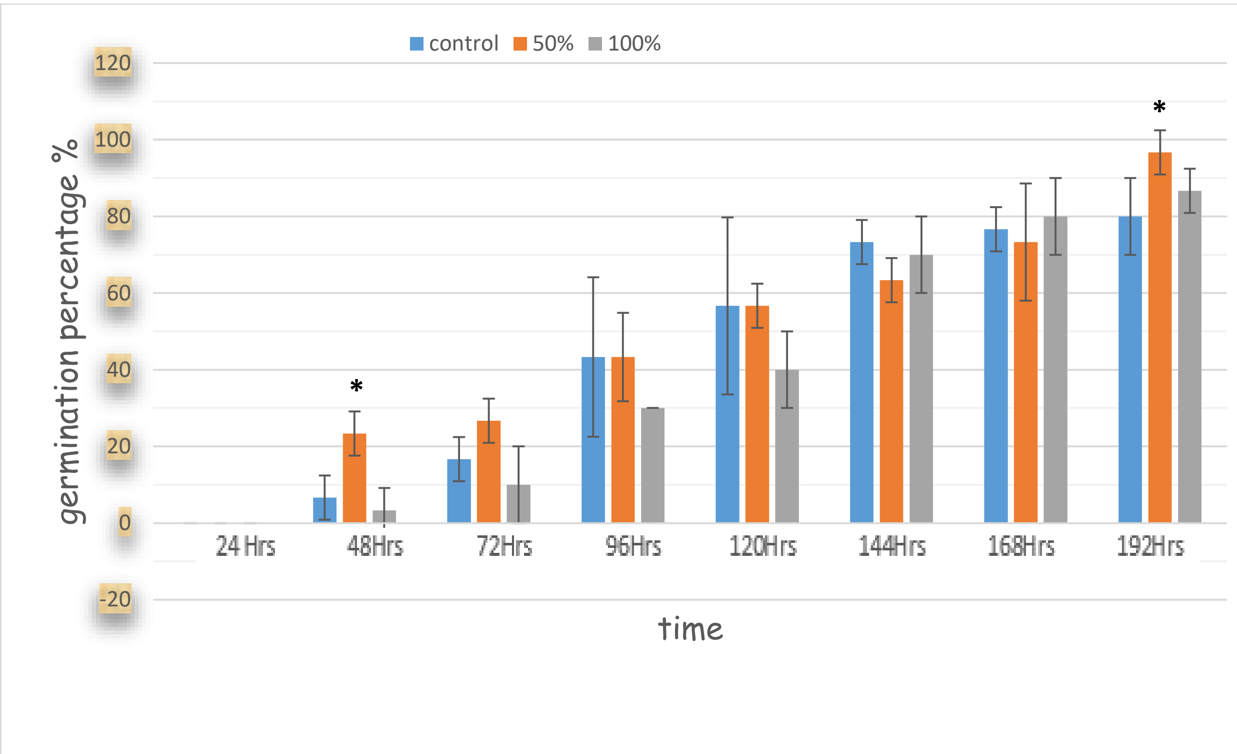

Figure 4.8 Effect of CA paint industry wastewater on the germination rates of tomato

The increment in the germination percentages increased with the increase of wastewater concentration and treatment duration. The treatment with 50% of wastewater for 192 h was more effective than the other concentrations and treatment duration. There was a statistically significant difference in germination percentage according to control. The maximum germination of seeds was observed at 50 % applied concentration of CA paint industry wastewater, after 48 h to exposure, where it reached up to 20%. (Figure 4.8) At higher concentrations (100%), a decrease in germination was observed that EC is too high can result in a physiological drought which restricts root water uptake by the plant, even when the substrate is moist and The germination percentage of the seedling under high osmotic pressure varies with seedling species and verities (Singh,et.al.,1985)

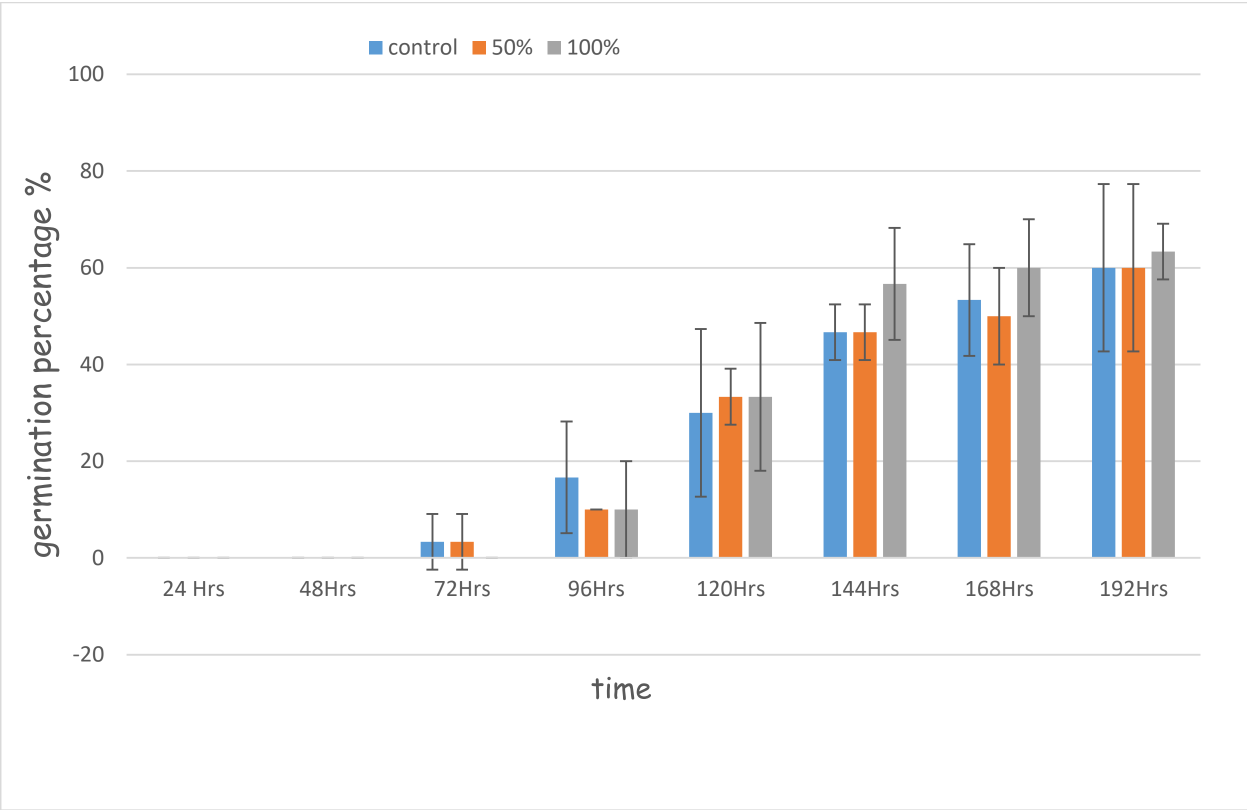

Figure 4.9 Effect of CA paint industry wastewater on the germination rates of D. carota (carrot).

The results presented in Figure 4.9 showed that the germination percentages in test plant were reduced by 50% and 100% applied concentrations as compared with control values. There was no germination in seeds of D. carota (carrot) until 72 hr. after sowing incase of 50% applied concentration and control. However 100% applied concentration of CA paint factory waste water, until 96hr there was no germination seen. All the tested concentrations of paint industry wastewater had no significant effect on germination in D. carota (carrot) as compared to the control (Fig. 4.9).

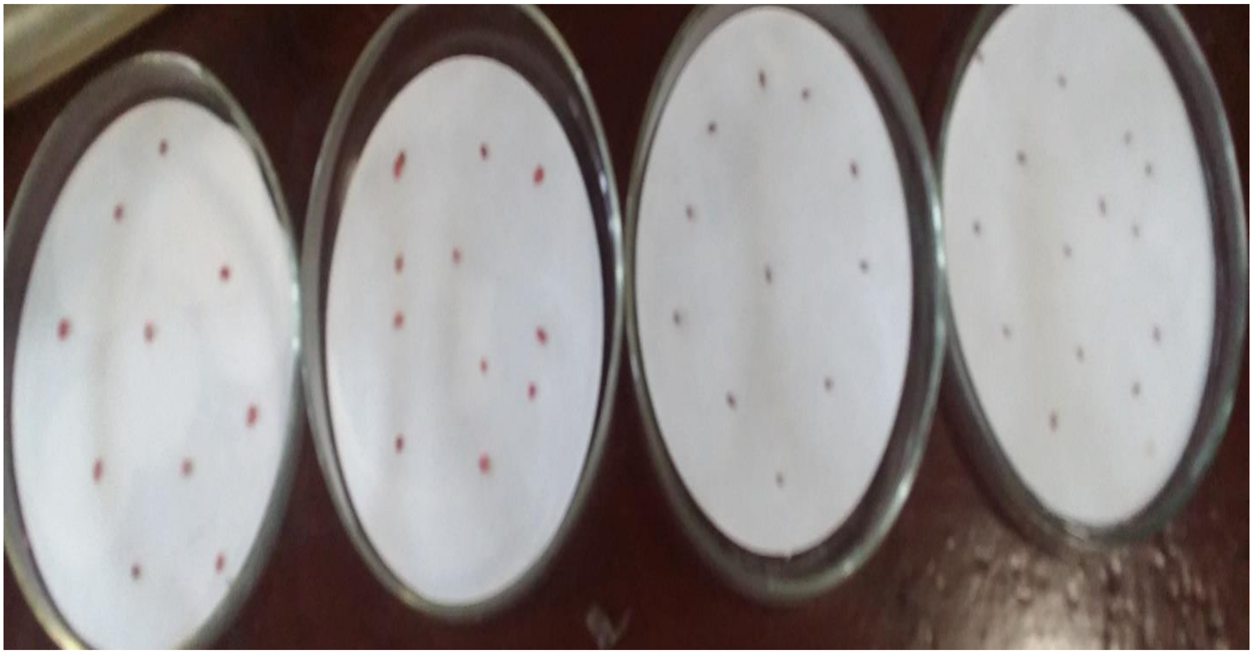

Figure 4.10 the seed (solanum lycopersicum (tomato) and D. carota (carrot)) irrigated with the paint waste water with applied concentration 50% and 100%

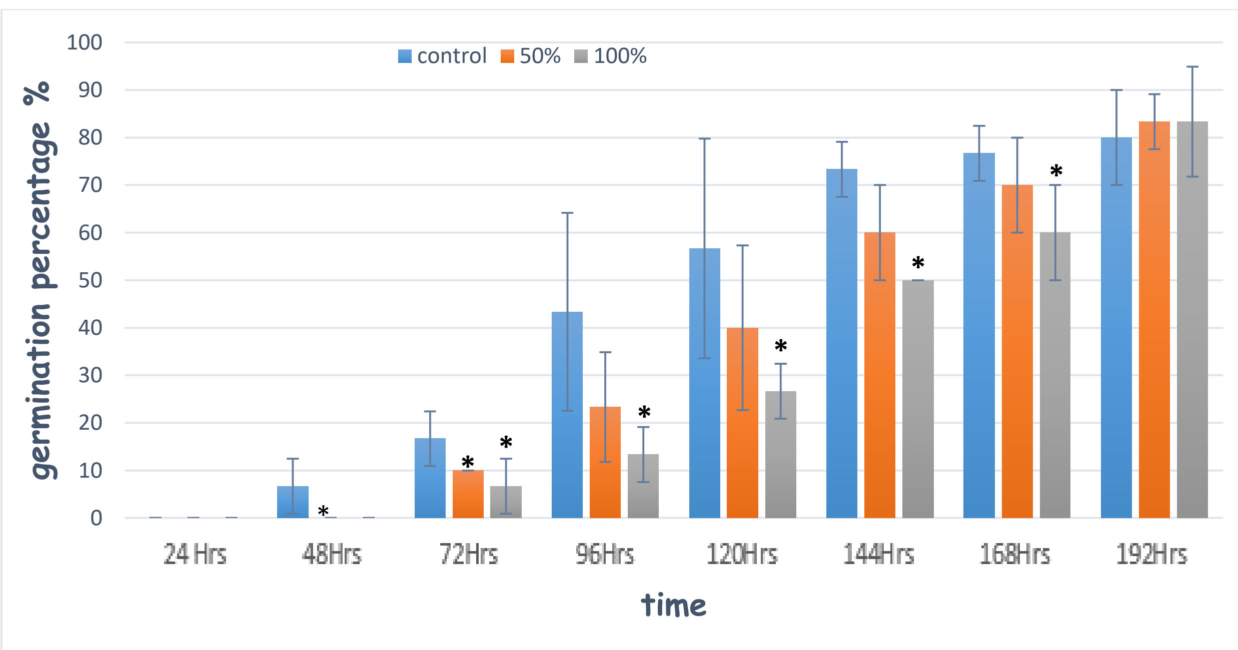

Figure 4.11 Effect of NS paint wastewater on the germination rates on tomato

There was no germination in seeds of solanum lycopersicum (tomato) until 72 hr. after sowing except the seed irrigated with control (Figure 4.10). There was a statistically significant difference in germination percentage according to control. At higher concentrations (100%), a decrease in germination was observed and this effect was statistically significant at 100 % applied concentration of wastewater in all time intervals except at 192 hrs. The seed growth and germination is inversely proportional to the concentration of the effluent used(Divya et al., 2015). The treatment with 50% applied concentration also decreases in germination. However 50% applied concentration wastewater had no significant effect on germination in solanum lycopersicum (tomato) as compared to the control. The decrease in efficiency of seed germination at higher concentration may be due to the higher osmotic pressure which retards the seedling growth. (Divya et al., 2015) (Ayyasamy, Banuregha, et al., 2008). reported that high osmotic pressures of the germination solution makes inhibition's more difficult and retards germination, while the ability of seeds to germinate under high osmotic pressure differs with variety as well as species.

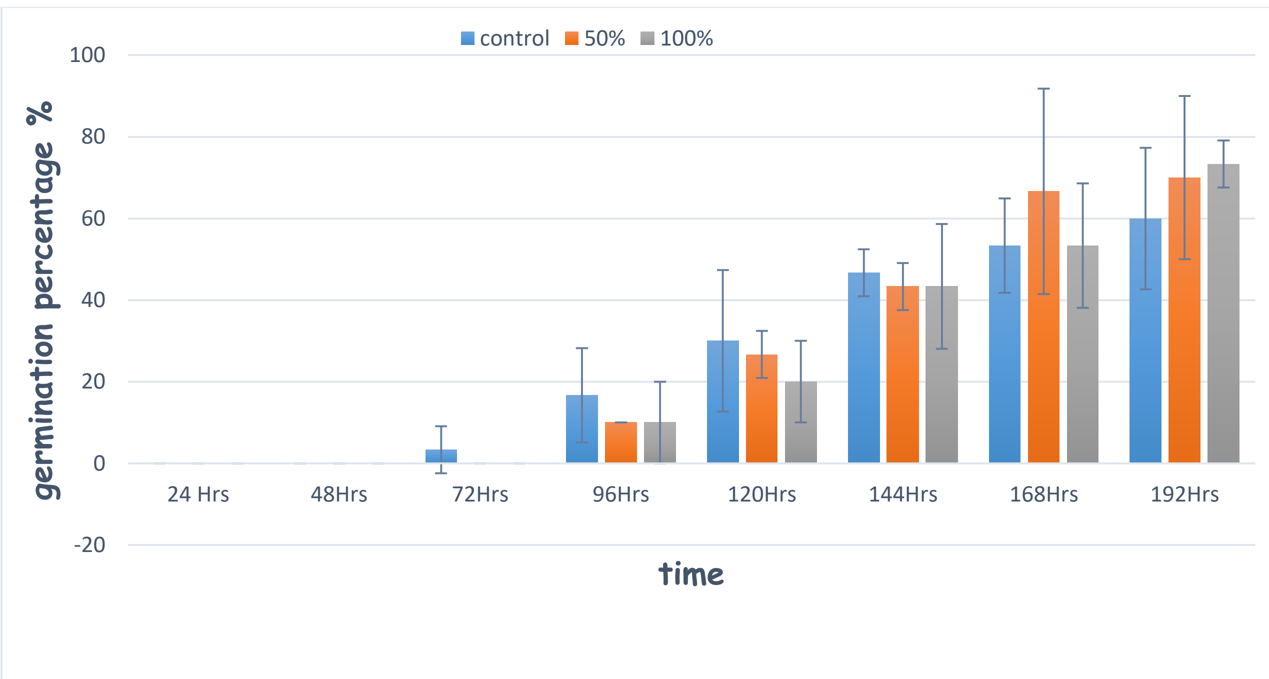

Figure 4.12 Effect of NS paint wastewater on the germination rates on D. carota (carrot).

There was no significant difference between the H_2O control and any of the 50% applied concentration and 100% applied concentration. There was no germination in seeds of D. carota until 72 h after sowing in case of both 50% and 100% applied waste water treatment. Some minor effects were detected in D. carota (carrot) seed germination upon exposure to paint industry wastewater, but there was no significant effect between the H_2O control and any of the Wastewater plant treatments. The increment of the germination percentages increased with the increase of wastewater concentration and treatment duration.

4.12 Effect of paint wastewater on growth

The effect of selected paint waste wastewater concentration on shoot and root growth was determined and shown in table and image.

Table 4. 3 The effect of the paint waste water on the vegetable growth

Values given are means ± standard deviation. Asterisks (*) show significant differences as compared to the control

		Control	CA		NS	
seeds		0%	50%	100%	50%	100%
Carrot	shoot	4.23±1.24	4.48±1.17	4.53±1.108	4.54±0.69	3.41±0.85
	Root	1.31±0.90	2.18±1.01	2.81±1.18*	1.95±0.73	1.07±0.84*
Tomato	Shoot	5.23±1.13	5.97±1.21	6.191±0.89	5.65±1.17	6.6± 1.15
	Root	9.16±2.56	9.23±1.76	6.26±2.79*	7.68±2.23*	8.45±2.08*

4.12.1 Effect of CA paint factory wastewater on growth

a. Solanum lycopersicum (tomato)

Solanum lycopersicum(tomato) vegetable grown on petridish irrigated with the concentrations of 50% and 100% effluent of CA paint factory showed increase in their mean value of heights(shoot and root) compared to the control plants. However A statistically significant difference was determined in root growth on 100% applied concentration of Cadisco paint waste water compared to control (table 4.2.) (Figure 4.13).

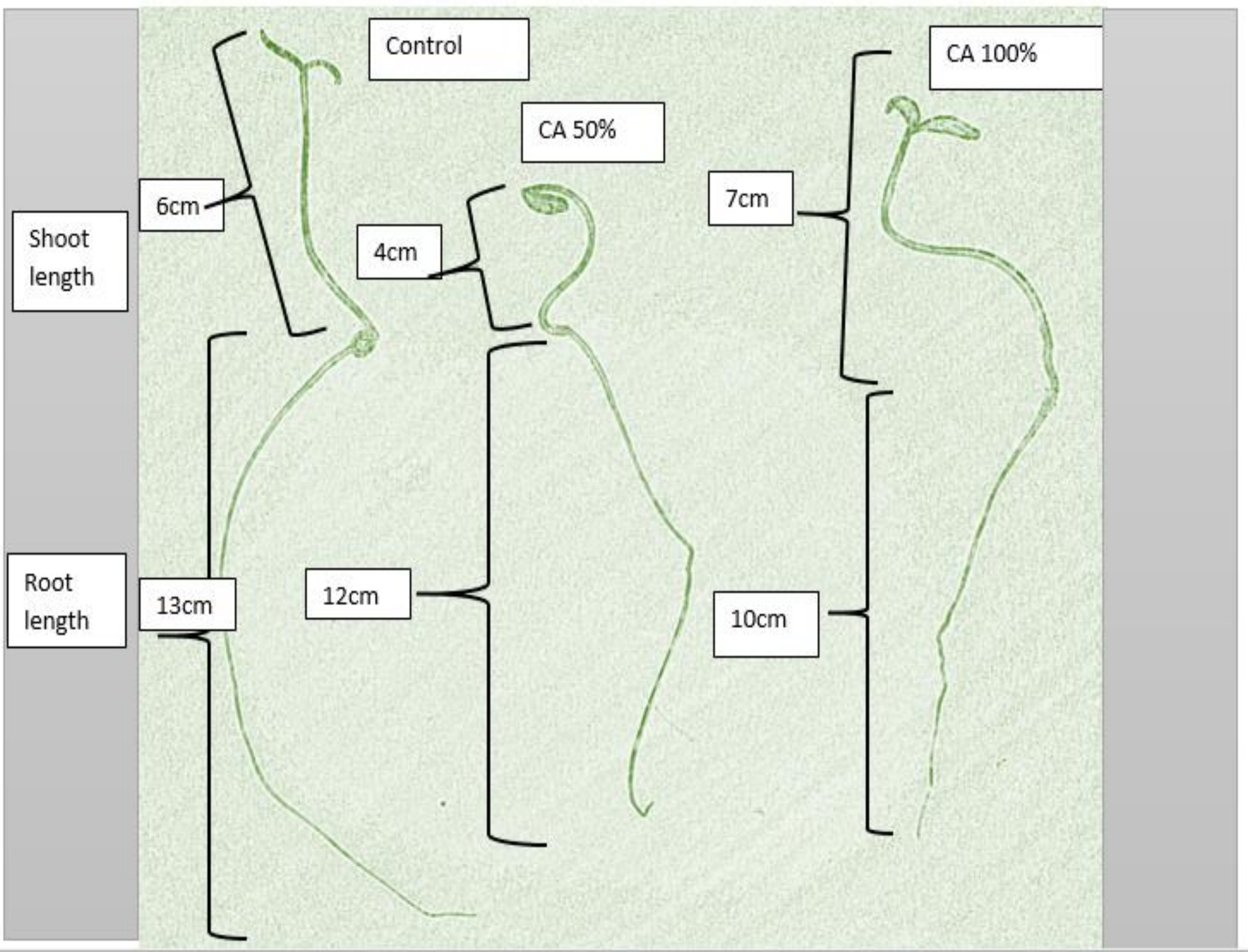

Figure 4.13 Effect of CA paint wastewater on the growth of Solanum lycopersicum (tomato) shoot and root

The high mean value of shoot lengths of Solanum lycopersicum(tomato) was observed in the 100% applied concentration, followed by effluent concentrations of 50% applied and control respectively (Table 4.2), with direct relationship between shoot length and effluent concentration. This is mainly because effluent is rich in nutrients and can significantly improve the growth of the seed content after being applied(Karunyal et al., 1994) . However, if the concentration of heavy metals in the sludge exceeds the upper limit that can be tolerated, plant growth will exhibit different degrees of inhibition (Almodares et al., 2007a). However, the maximum shoot length was found 100 % applied concentration (7cm) and the minimum shoot length (4cm) of the seed was found in irrigated by 50 % applied concentration of CA paint factory wastewater (Figure 4.14) .

The high mean value of root lengths of Solanum lycopersicum (tomato) were observed in 50% applied concentration compared to control and 100% effluent concentration. Dilution has been shown to be effective in some cases, including reducing ammonia volatilization following land application of animal manures (Moore & Moore, 1976). The seed irrigated with concentrations of 100% was significance difference compered to control (Table 4.2). the maximum root lengths of Solanum lycopersicum(tomato) was observed in control.(13m) and the minimum was found in 100% applied concentration CA paint factory waste water (10cm) (Figure 4.15).

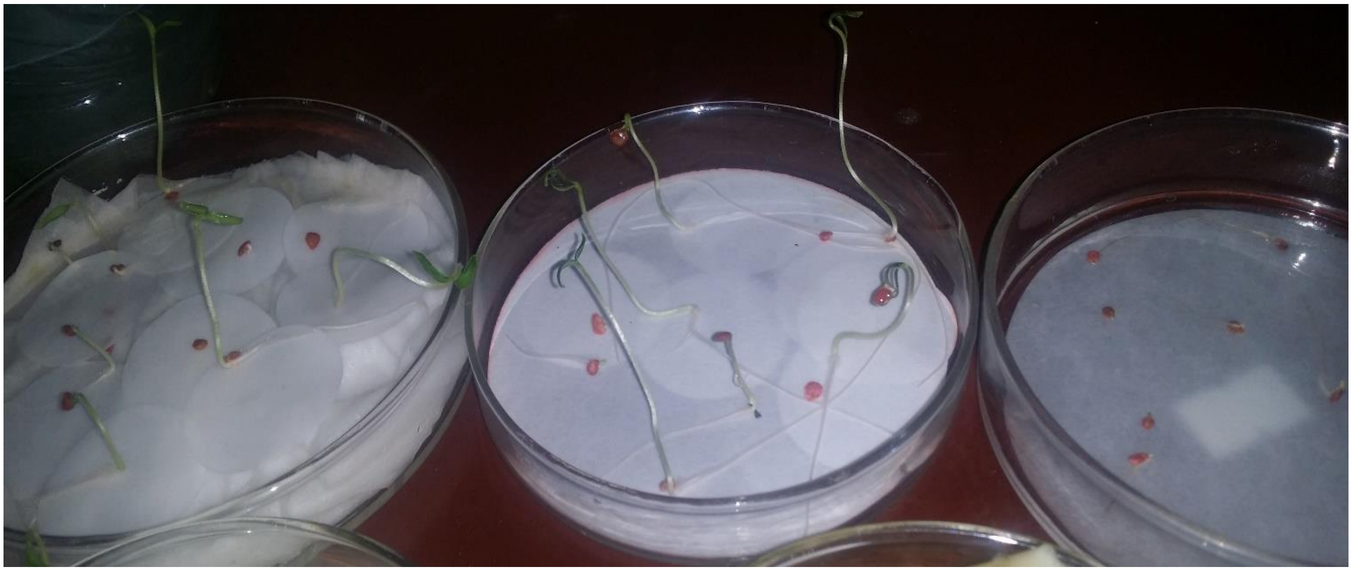

Figure 4.16 when the Solanum lycopersicum (tomato) is growing in petri-dish

b. D.carota (Carrot)

The mean value of shoot lengths of D.carota increased when the concentration of the waste water is increased with direct relationship between shoot length and effluent concentration like Solanum lycopersicum (tomato). However, there is no statistically significant difference determined in shoot growth, irrigated by 50 % and 100% applied concentration of cadisco paint waste water compared to control (table 4.2) (Figure 4.17).

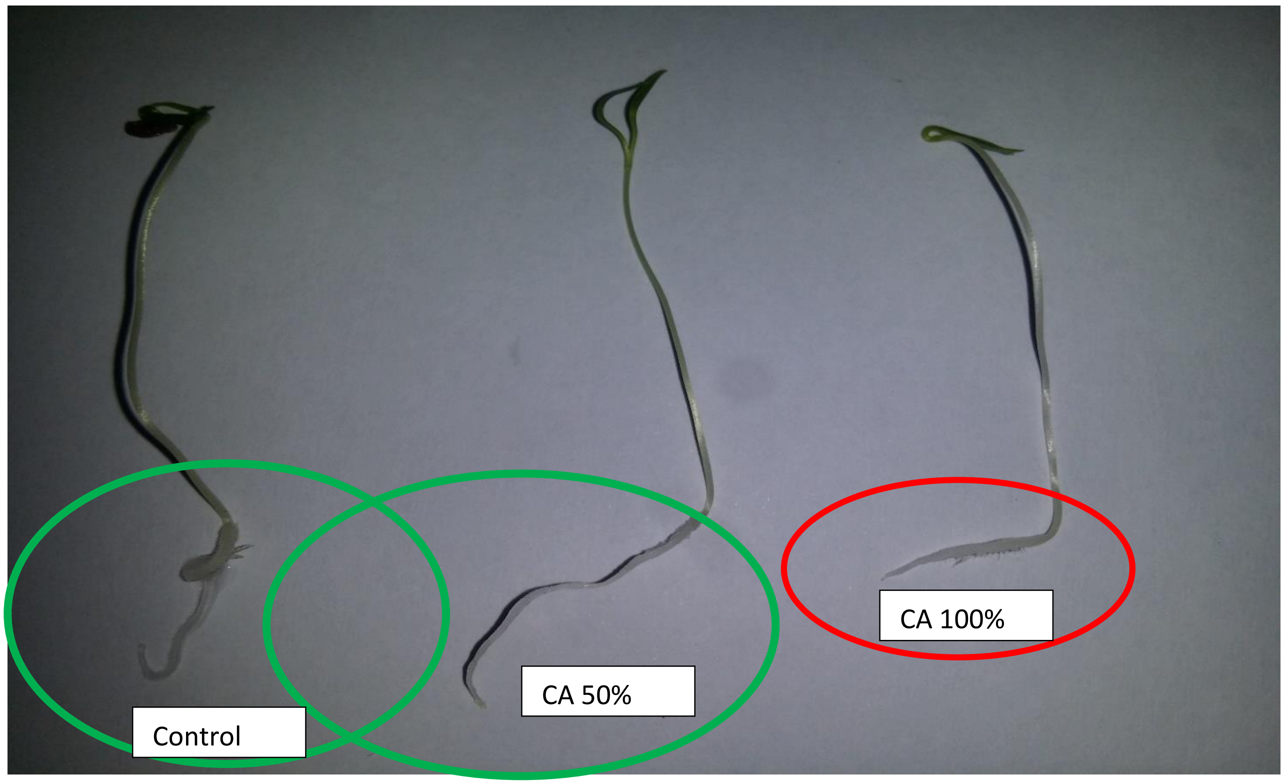

Figure 4.18 Effect of CA paint wastewater on the growth of D.carota (Carrot) shoot and root

This is mainly because effluent is rich in nutrients and can significantly improve the growth of the seed content after being applied(Karunyal et al., 1994) May be Cadisco paint waste water relevant to irrigated waste water quality and the water However the maximum shoot length was found 50 % applied concentration (6cm) and the minimum shoot length (3cm) of the seed was found in irrigated by 100 % applied concentration of Kadisco paint factory wastewater (Figure 4.15) .

The mean value of root lengths of D.carota increased when the concentration of the waste water is increased with direct relationship between root length and effluent concentration. The seed irrigated with concentrations of 100% applied was significance difference compered to control

(Table 4.2), the maximum root lengths of D.carota was observed in control (9cm) and the minimum was found in 100% applied concentration CA paint factory waste water (4cm).

4.12.2 Effect of CA paint factory wastewater on growth

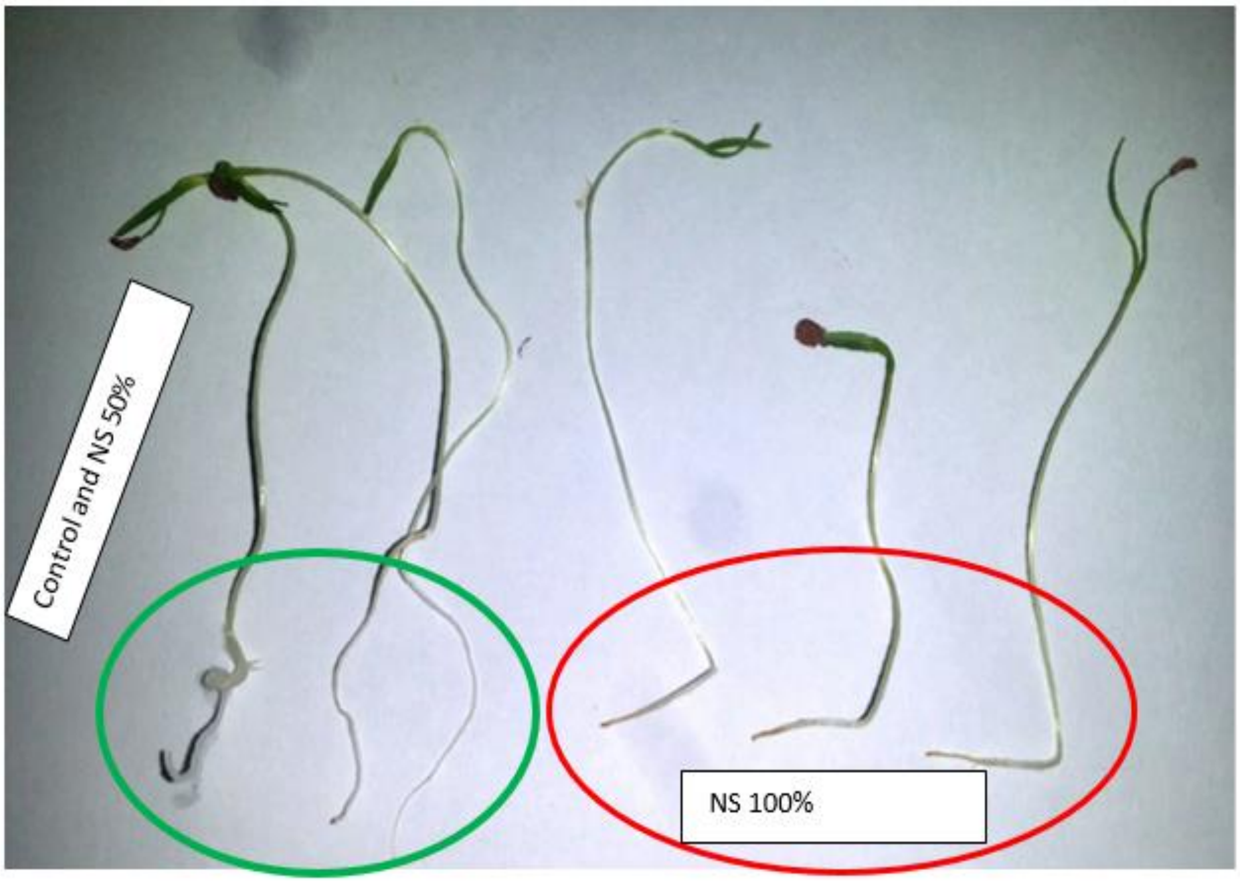

Figure 4.19 Effect of NS paint wastewater on the growth of D.carota (Carrot) shoot and root

a. D. carota (carrot)

The root of D. carota (carrot) severely affected by the higher effluent concentrations (100%) compared to the control and 50% applied concentration. As shown on the Figure 4.16. No any root of the D.carota growth properly and it look like the burned root with fire. The means of D. carota (carrot) root length applied 100% concentrations were significantly lower than the control. Thus, Salt accumulation in the root zone causes the development of osmotic stress and disrupts cell ion homeostasis by inducing both the inhibition in uptake of essential elements such as $K+$, $Ca\ 2+$, and $NO3\ −$ and the accumulation of $Na+$ and $Cl−$ (Hashem & Qi, 2021). Specific ion toxicities are due to the accumulation of sodium, chloride, and/or boron in the tissue of transpiring leaves to damaging levels. Accumulation of injurious ions may inhibit photosynthesis and protein synthesis, inactivate enzymes, and damage chloroplasts and other organelles (Machado & Serralheiro, 2017) The heavy metal pollution interferes with the uptake of K, Mg, S, P, Ca, Fe, Mn, Zn and Cu and affects their translocation from roots to tops, which reduces the elements essential for plant growth.

Salt decreases crop yields by reducing growth and inducing leaf senescence due to both an osmotic stress (plant water deficit) and an ionic stress provoked by nutritional imbalances and the accumulation of toxic ions such as sodium (Munns and Tester, 2008). Other researchers have reported that salt stress resulted in a reduced cell turgor and depressed rates of root and leaf elongation (Fricke et al. 2006). It has been reported that high concentrations of wastewater result on strong prohibition of seeds and seedling growth (Casa et al. 2003; Komilis et al. 2005).

b. Solanum lycopersicum (tomato)

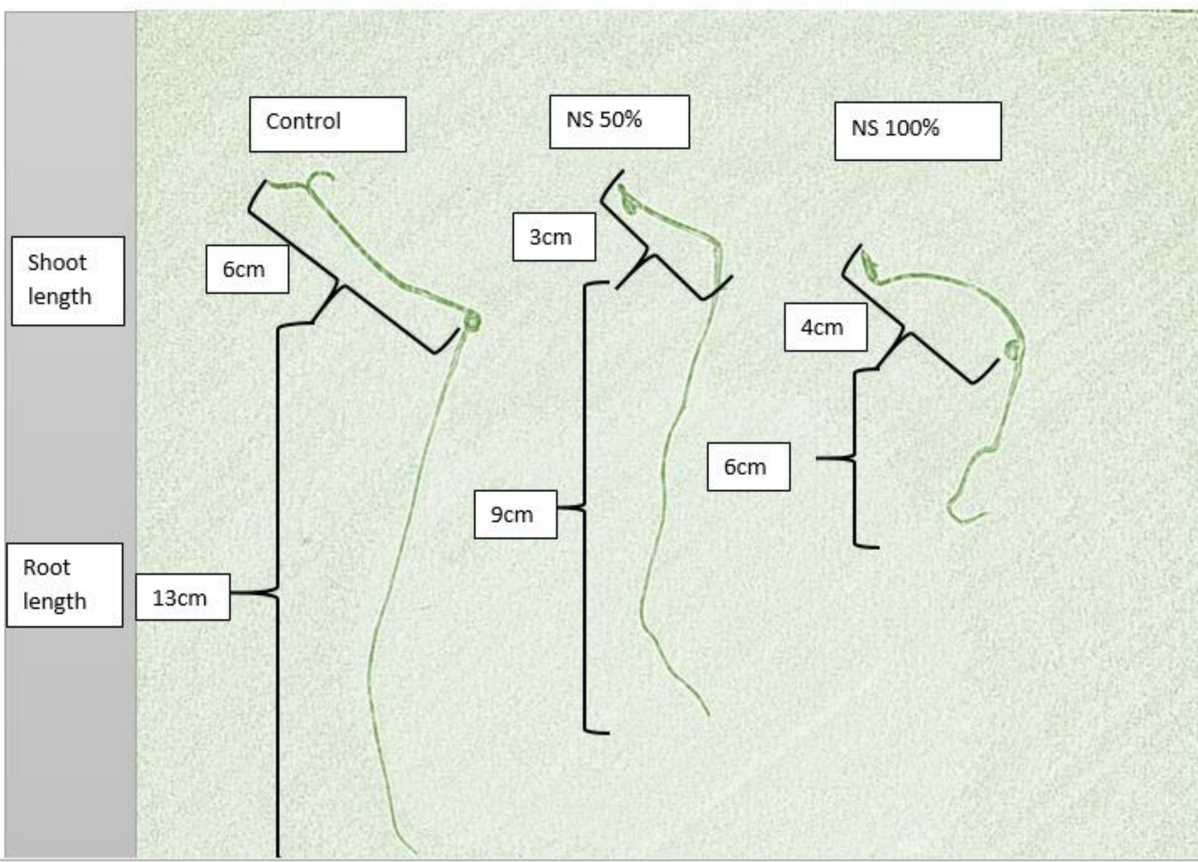

Figure 4.20 Effect of NS paint wastewater on the growth of Solanum lycopersicum (tomato shoot and root

The mean value of shoot length of the seedlings vary with the concentration of the treated sewage waste water. The mean length of all the seedling (Solanum lycopersicum (tomato) increased with the increase in concentration of the effluent. However, there is no statistically significant difference determined in shoot growth on 50 % and 100% applied concentration of NS paint waste water compared to control (table 4.2.) Figure 4.21. The maximum shoot length was found in control (6cm) (image 4.5) however, the root length of the (Solanum lycopersicum (tomato) was severely influenced by various concentrations of effluent. Maximum root length was observed in control which was 13 cm for (Solanum lycopersicum (tomato). In the case of 50% and 100% effluent, the maximum root length was found to be 9 and 6 cm respectively (Table 4.2). The high mean value of root lengths of Solanum lycopersicum (tomato) was observed in control. All the tested concentrations of NS paint industry wastewater had significant effect on growth of (Solanum lycopersicum (tomato) as compared to the control. Germination is believed to be the most sensitive and vulnerable to water availability and to the salinity and toxic compounds of the growth medium (Khan & Jan, 2011). Moreover, salt concentration reduces the germination rate ((Almodares et al., 2007b); (Dennis W. & Robert S., 2019). This is an important phenomenon as the seeds that germinate faster can make use of the limited soil water and establish seedlings, which is less sensitive to stress conditions, before stress conditions prevail (Rusan et al., 2015). Other researchers have reported that salt stress resulted in a reduced cell turgor and depressed rates of root and shoot elongation(Divya et al., 2015)(Rusan et al., 2015). It has been reported that high concentrations of effluent result on strong prohibition of seeds and seedling growth (Karunyal et al., 1994).

5. CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusion

This research illustrates that many paint factories in Ethiopia do not treat their effluent before discharge into the environment due to their incapability to afford good effluent treatment plants, while the Waste Water Treatment Plants of the ones that could afford treatment are not efficient enough to bring about effluents that are eco-friendly. The effluents released to the surrounding from the treatment paint factories wastewater contain some physicochemical parameters higher than the standards given by the ES and/or WHO. The results obtained also CA paint industry performed better than others based on the percentage reduction efficiencies of the WWTPs used in all the studied paint companies, while NS paint factory had the least performance. This study revealed that WWTPs of the three selected paint factories which are representatives of paint companies in Addis Ababa are ineffective in removing TDS and EC. Also in terms of BOD and COD parameters, they are ineffective (except CA paint industry). Hence effluents generated by the paint factories serve as one of the major pollution sources of the water bodies. As a result, shown waste wastewater originating from paint factories have different effects on different vegetables, depending upon the nature of the effluent. NS paint industry wastewater contains appreciable concentrations of BOD, COD, suspended solids, toxic compounds (toxic heavy metal compounds) compared to CA paint factory waste water and had high effect on germination and growth of shoot and root, while CA paint industry wastewater had a stimulatory effect on germination and growth (shoot and root) rate of seeds. So the paint wastewater contains appreciable concentrations of BOD, COD, suspended solids, toxic compounds (toxic heavy metal compounds) which reduce the growth and germination potential of carrot and tomato seeds, especially at high EC and TDS.

5.2 Recommendation

- It is recommended that restricted waste minimization for paint industries be enforced by EFCCC. It is expected that this waste reduction at source approach will promote waste recycling, protect public health and the environment.
- To solve the problem in a sustainable way, these factories should have to apply secondary and tertiary treatment plants in good manner and follow the right procedures to treat the

waste water by applying accurate amounts of chemicals, good maintenance, preparing good environmental management plan and continuous checking and evaluation before releasing their effluent to the nearby rivers.

- The future research may include the impact of long term application of paint waste water on human health and regular monitoring of toxic heavy metals in vegetables by concerned bodies is vital to prevent disproportionate build up in the food chain.
- To avoid entrance of metals into the food chain, a green treatment technique, such as a constructed wetland, should be used as a method to reduce heavy metal concentrations from wastewater drained from paint factories.

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7. APPENDICES

Appendix 1 Mean Value of Trace metal and physicochemical parameters analyses results

		PO_4^{3-}	NO_3^-	SO_4^{2+}	NH_3	NH_4^+	COD	BOD	Cr^{+6}	Zn^{+2}	cd	pb
C1	1	35.10	37.26	1350.00	36.30	38.70	659	154.65	BDL	1.00	BDL	1.02
	2	34.20	24.30	1350.00	36.30	38.70	648.00	148.60				
	3	33.30	0.63	1620.00	36.30	38.70	654.00	151.62				
	Mean v	34.20	20.73	1440.00	36.30	38.70	653.67	151.62				
C2	1	1.36	11.30	142.00	0.38	0.40	281.00	6.50	BDL	0.02	BDL	0.06
	2	1.20	13.70	138.00	0.33	0.35	286.00	5.40				
	3	1.84	12.50	140.00	0.28	0.30	282.00	7.30				
	Mean v	1.47	12.50	140.00	0.33	0.35	283.00	6.40				
NF1	1	5.49	2.85	441.00	3.28	3.84	533.00	179.20	BDL	1.03	BDL	1.09
	2	5.13	2.85	567.00	2.80	2.96	535.00	183.20				
	3	4.95	2.85	486.00	2.48	2.72	536.00	175.60				
	Mean v	5.19	2.85	498.00	2.85	3.17	534.67	179.33				
NF2	1	0.80	0.88	185.00	0.45	0.48	325.00	34.83	BDL	0.01	BDL	0.01
	2	1.04	0.44	190.00	0.45	0.48	321.00	38.24				
	3	2.08	0.72	190.00	0.39	0.41	322.00	34.21				
	Mean v	1.31	0.68	188.33	0.43	0.46	322.67	35.76				
Z1	1	24.30	17.80	1400.00	7.50	8.10	715.00	271.77	BDL	1.05	BDL	1.05
	2	12.35	16.29	1088.00	7.50	8.10	720.00	280.80				
	3	22.50	17.10	1240.00	7.50	8.10	725.00	273.50				
	Mean v	19.72	17.06	1242.67	7.50	8.10	720.00	275.36				
Z2	1	1.04	0.77	26.00	0.41	0.44	490.00	34.82	BDL	0.02	BDL	0.06
	2	1.92	0.77	33.00	0.35	0.37	484.00	37.23				

	3	1.60	0.77	38.00	0.41	0.44	481.00	34.20				
	Mean v	1.52	0.77	32.33	0.39	0.42	485.00	35.42				

Hint; - 1 for wastewater before treatment and 2 is stand for waste water after treatment plant

Appendix 2 Percentage Reduction Efficiencies

Code	$PO4^{3-}$	NO_3^-	$SO4^{2+}$	NH3	NH_4^+	COD	BOD	pb	Zn^{+2}
CA 1	34.20	20.73	1440.00	36.30	38.70	653.67	151.62	1.02	1
CA2	1.47	12.50	140.00	0.33	0.35	283.00	6.40	0.06	0.02
efficiency	95.71	39.70	90.28	99.09	99.10	56.71	95.78	98	98.00
NS1	5.19	2.85	498.	2.85	3.17	534.67	179.33	1.09	1.03
NS2	1.31	0.68	188.33	0.43	0.46	322.67	35.76	0.01	0.01
efficiency	74.82	76.14	62.18	84.93	85.61	39.65	80.06	99.1	99.03
ZE 1	19.72	17.06	1242.67	7.50	8.10	720.00	275.36	1.051	1.05
ZE 2	1.52	0.77	32.33	0.39	0.42	485.00	35.42	0.06	0.02
efficiency	92.29	95.4	97.3980	94.8	94.855	32.63	87.13	98.7	98.09524

Appendix 3 Environmental Standards for Industrial pollution for paint industries

Standards	PO_4^{3-} (mg/l)	NO_3^- (mg/l)	SO_4^{2+} (mg/l)	pH	TDS (mg/l)	EC (mS/m)	COD (mg/l)	BOD (mg/l)	Cr^{+6} (mg/l)	Zn^{+2} (mg/l)	Cd (mg/l)	Pb (mg/l)	Reference
ES	10	-	-	5.5 – 9.5	3000	-	-	-	0.1	1	0.2	0.5	(Berihun & Solomon, 2017b)
WHO	15	45	300	6 – 9	1500	150	120	60	0.05	0.2	0.01	0.01	(Aniyikaiye et al., 2019) (WHO,2006)

Appendix 4 Paint Industrial waste water and Irrigation Water Quality Standards

Water Quality Classification	EC at 25 °C (mS/m)	TDS (mg/L)	SAR (meq/L)	RSC (meq/L)
Excellent	<250	500-1500	Up to 10	<1.25
Good	<160	2250-4000	10-18	1.25-2.5
Medium	250-750	1500-2500	18-26	>2.5
Bad	160-500	>4000	>26	-
Very Bad	750-2250	>2500	>26	-

Appendix 5 Recorded Germination and GP of the seed, irrigated with Cadisco and Nifas Silk paint factories wastewater

		Time interval (Hrs or days)								
Treatments	**Replication**	**24 Hrs**	**48Hrs**	**72Hrs**	**96Hrs**	**120Hrs**	**144Hrs**	**168Hrs**	**192Hrs**	**GP%**
	R1	0	1	2	6	7	7	7	7	70
Tom1/control	R2	0	1	2	5	7	8	8	9	90
	R3	0	0	1	2	3	7	8	8	80
	R1	0	2	2	3	5	6	6	10	100
cad Tom/50	R2	0	2	3	5	6	6	9	9	90
	R3	0	3	3	5	6	7	7	10	100
	R1	0	0	0	3	5	7	7	8	80
cad Tom/100	R2	0	0	1	3	4	8	8	9	90
	R3	0	1	2	3	3	6	9	9	90
	R1	0	0	1	3	5	5	6	7	70
car/control	R2	0	0	0	1	2	4	4	4	40
	R3	0	0	0	1	2	5	6	7	70
	R1	0	0	0	1	3	5	5	5	50
ca car/50	R2	0	0	0	1	3	4	4	5	50
	R3	0	0	1	1	4	5	6	8	80

	R1	0	0	0	0	3	5	6	6	60
ca car/100	R2	0	0	0	2	5	7	7	7	70
	R3	0	0	0	1	2	5	5	6	60
	R1	0	0	1	3	5	5	7	8	80
Ni to/50	R2	0	0	1	1	2	6	6	8	80
	R3	0	0	1	3	5	7	8	9	90
	R1	0	0	0	2	3	5	5	7	70
Ni to/100	R2	0	0	1	1	3	5	7	9	90
	R3	0	0	1	1	2	5	6	9	90
	R1	0	0	0	1	2	4	4	5	50
Ni car/50	R2	0	0	0	1	3	5	7	7	70
	R3	0	0	0	1	3	4	9	9	90
	R1	0	0	0	1	2	6	7	7	70
Ni car/100	R2	0	0	0	0	1	3	4	7	70
	R3	0	0	0	2	3	4	5	8	80