ADDIS ABABA UNIVERSITY

DEPARTMENT OF CHEMISTRY

Determination of Heavy Metal (Cr, Cd, Pb, Ni) Concentration in Paint Industry Effluent in Addis Ababa Ethiopia by Flame Atomic Absorption Spectroscopy (FAAS)

A Thesis Submitted to the Department of Chemistry Addis Ababa University in Partial Fulfillment of the Requirements for a Master of Science in Chemistry

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ABBREVIATION

AAS	Atomic Absorption Spectroscopy
APHA	American Public Health Association
ATSDR	Agency for Toxic Substances and Disease Registry
DWAF	Department of Water Affairs and Forestry
EPA	Environmental Protection Agency
ES	Ethiopian Standard
FAAS	Flame Atomic Absorption Spectroscopy
FDRE	Federal Democratic Republic of Ethiopia
GFAAS	Graphite Furnace Atomic Absorption Spectroscopy
IARC	International Agency for Research on Cancer
IUPAC	International Union of Pure and Applied Chemistry
ppm	parts per million
WHO	World Health Organization

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ABSTRACT

Heavy metals pollution is a major problem in both developed and developing countries. In Ethiopia, the wastewater in most of the paint industries is not treated properly, but instead is fed directly into rivers. Recently, there are more paint industries in Ethiopia, polluting the environment and posing public risk from the release of untreated waste. This industrial sewage pollutes the nearby bodies of water and affects the growth of vegetation. These toxic heavy metals, when released into the aquatic environment, enter the food chain and cause various health problems in humans. This research work deals with the determination of toxic heavy metals in industrial effluents from four paint industries. The overall results indicate a high concentration of heavy metals in the effluents samples from four different paint industries.The study reveals that the Kadisco and Abay paint industries were the major contributors of toxic heavy metals, particularly Cr, Cd, Pb, and Ni in the surrounding. The paint industry in Addis Ababa contributes to the pollution of the river water. Major contributors include the Nefas silk paint factory which released 5.602 mg/L toxic cadmium, the Kadiscopaint factory which released 1.781 mg/L chromium and an average of 0.8101 mg/L lead. The paint factory Abay released an average value of 4.261 mg/L nickel. All indicated values were above the permissible limit value of the ES EPA and the WHO.

Keywords: Heavy metal, Paint industry, Effluent, Wastewater

1. Introduction

Heavy metals pollution is a major problem in both developed and developing countries. Pollution is a matter of great concern and has been accepted as a global problem because of its negative effects on human health, plants, and animals. Heavy metals such as cadmium, lead, chromium, nickel, and mercury are the main pollutants [1]. Among the environmental pollutants, heavy metal toxicity has received special attention globally, even at a lower level, because of its neurotoxicity, carcinogenicity, and several other adverse effects [2].

The effluent from a paint industry is one of the causes of water pollution. Paint is generally considered to be a mixture of pigments, binders, additives, and proportion of each component in the mixture that characterize the properties of a particular paint. The components of the paint also determine the properties of the waste generated during its production and use. The discharge of such wastewater with high pollutants into the environment is detrimental to the quality of the water bodies and also affects the food chain, so it is essential to treat the wastewater before it is disposed of [3].

Water-based paints generally consist of organic and inorganic pigments and dyestuffs, extenders, cellulosic and non-cellulosic thickeners, latexes, emulsifying agents, antifoaming agents, preservatives, solvents and coalescing agents [4]. The paint effluent is characterized by a high content of organic matter, a high salt content, high sulfate content and high suspended solid [5].

Untreated industrial wastewater from paints contains varying amounts of heavy metals such as arsenic, lead, nickel, cadmium, copper, mercury, zinc and chromium [6], which have the potential to contaminate plants growing under such irrigation. These heavy metals have a strong influence on the aquatic flora and fauna that enter the food chain and ultimately affect humans. Heavy metal pollution is a growing problem in our oceans, lakes and rivers. The accumulation of heavy metals in fish, oysters, sediments and other components of aquatic ecosystems has been reported worldwide [7].

These toxic heavy metals that get into water are adsorbed on particulate matter. They can form free metal ions and soluble complexes that can be taken up by biological organisms [8].

The wastewater arises primarily from the cleaning operation of mixers, reactors, packaging machines and floors [9]. Several methods have been developed to decontaminate industrial effluent. Various heavy metal removal processes include chemical precipitation, membrane filtration, electrolytic processes, adsorption and coagulation flocculation. Adsorption processes for effluent purification have gained great interest in recent years for their efficiency in removing pollutants, particularly heavy metal ions, colors, odors and organic contaminants [10]. The enormous increase by industrial pollutants has led to a systematic and detailed investigation of pollution by toxic heavy metals in effluent samples from the paint industry in Addis Ababa, which is considered to be one of the fastest developing industrial zones in Ethiopia [11].

1.1. Statement of the problem

The effluent from the paint industry contains high levels of organic and inorganic toxic substances such as BOD, COD, TSS, TDS, turbidity, colored material and heavy metals [12]. These have serious negative effects, not only on surface water and groundwater, but also on aquatic ecosystems and humans. In Ethiopia, most of the paint industries do not treat the effluent properly, but instead discharge it directly into the river [13]. Recently, there have been more paint industries in Ethiopia that pollute the environment and pose public risk from the release of untreated waste [14].

The soil and water ecosystems around the world have been contaminated with heavy metals from various human activities, and the transport of metals in the food chain has become a threat to human health [15]. As a result, human activities also increase the concentration of heavy metals in soils and plants as a decrease in the productivity of crop land productivity. The environment and the Akaki River receive untreated domestic sewage from residential areas and industrial effluents and then the local farmers use this effluent for agricultural purposes around the Akaki River before the contaminated effluent enters the river without any treatment at work. In addition, farmland produce could be contaminated as farmers wash them with contaminated water before putting them on the market. Kadisco, Nefas silk, Zemilli, and Abay paint industry effluents flowing through larger communities become heavily polluted when widely used for household, commercial and industrial purposes. The aim of this work was to determine the heavy metal concentration in wastewater from the paint industry.

1.2. Objectives

1.2.1. General objective

The main objective of this study was to determine the concentration of heavy metals (Cr, Cd, Pb and Ni) in waste water from the paint industry in Addis Ababa, Ethiopia, by using flame atomic absorption spectroscopy.

1.2.2. Specific objectives

- To determination the concentrations of toxic metals (Cd, Cr, Ni and Pb) by means of FAAS in the four different waste waters of Kadisco, Nefassilk, Zemilli and Abay paint industries.
- To compare the concentration of cadmium, chromium, nickel and lead with the WHO and ESEPA

1.3. Significance of the study

The main aim of the study is to provide specific information about the heavy metals concentration in effluents from paint industries. It also shows to main sources of wastewater contamination. The results of this study can also be used as baseline information for industry owners to deploy low-cost waste water treatment technologies to minimize the percentage of heavy metals which polluting the nearby river and soil. Furthermore, to inform the city council to control the paint industries how they discharges the contaminated water into the environment and to control its waste treatment method and to inform farmers about the toxic effects of heavy metals on human health.

The potential hazard from the accumulation of metals from plants grown on contaminated soil is becoming an increasing problem in many countries, as are food safety issues and potential health risks from the accumulation of heavy metals in soils, water and plants one of the biggest problems is serious environmental concerns from environmentalists and health practitioners. This has created a demand for an intensive research effort aimed at predicting the availability of

heavy metals in the waste water. Particular attention should be paid to toxic metals such as chromium, nickel, cadmium and the most widely consumed agricultural crops [16].

Heavy metals such as cadmium and lead pose a risk to human health as they are not degradable pollutants and have a broad spectrum of activity (e.g. therefore a better understanding of heavy metal sources, their concentration and accumulation and the effect of their presence in water [17].

2. Literature review

2.1 Heavy metals

Heavy metals are defined as metallic elements that have a relatively high density compared to water. Many different definitions have been proposed, some based on density, some based on atomic number or atomic weight, and some based on chemical properties or toxicity, assuming that heaviness and toxicity are related. Heavy metals also include metalloids such as arsenic, which can cause toxicity with low exposure. Heavy metals are mainly used as pigments and additives in paint. The presence of these heavy metals is directly and indirectly dangerous for humans [18].

However, lead, cadmium, mercury and arsenic are the main threats to human health when exposed. Heavy metals such as cadmium, nickel, chromium and lead pose a number of hazards to humans; and are in fact cofactors as activators in biochemical and enzymatic reactions to inform the enzyme/substrate-metal complex [19]. Heavy metals are natural components of the earth's crust and are persistent environmental pollutants because they cannot be easily broken down or destroyed [20].

2.1.1. Heavy metals in the environment

Heavy metals exist in the solid phase and in solution, as free ions or are adsorbed on colloidal soil particles. In our environment there are many heavy metals such as iron, cobalt, copper, manganese, nickel and zinc etc., which act as micronutrients in lower concentrations or in small amounts.

These heavy metals are actually necessary for good health or are nutritionally essential for living organisms for a healthy life, beings such as Cu, Fe, Mn, Co and Zn are essential in certain physiological because of their involvement as micronutrients for life processes in plants, microorganisms and humans Processes. However, if the concentrations of these metals are above the recommended limit values or elevated values, their role changes into a negative dimension and these have proven to be toxic [21].

The potential toxicity and biotoxic effects of heavy metals result from the fact that they are transition elements that can form stable coordinated compounds (which are non-degradable) with a range of organic and inorganic ligands, and it has been suggested that their effects depend on the concentrations and oxidation levels of heavy metals, type of sources and type of deposition. Many metals act as biological poisons even in ppb. Some heavy metals are important in maintaining the metabolism of the human body. However, in higher concentrations they can lead to poisoning. Prolonged intake of toxic elements has harmful effects on humans and other animals [22].

That is, large amounts of any of them can become toxic or cause acute, chronic toxicity, or are often cytotoxic if they are not metabolized by the body and accumulate in the soft tissues, or if their deficiency can lead to a variety of diseases. The toxic metals and their ions are not only potential health hazards for humans, but also for other forms of life. Toxic metal ions cause physical discomfort and sometimes life-threatening illness, including irreversible damage to the body's vital system [23].

Heavy metals such as lead, cadmium and chromium are eco-toxicologically most dangerous. In many cases, the effects of heavy metals on humans are not well understood. Metal ions in the environment accumulate along the food chain. Cadmium has a lifespan of 10-30 years and its accumulation in the human body affects kidneys, bones and also causes cancer. Chromium compounds are naturally carcinogenic. As a result of increasing awareness of the toxicity of lead, its widespread use in various industries has been discontinued. Nickel is widely used in many industrial applications, e.g. in ship-building, automotive, electrical, oil, food and chemical industries. Although it is toxic to humans and animals in any concentrations [24]

In addition, long-term irrigation with contaminated wastewater or untreated or poorly treated wastewater, mainly from industrial sources, can lead to an accumulation of heavy metals in agricultural soils and crops. Recent developments in toxicities and other disorders resulting from ingestion and dietary of toxic metals in food have forced food regulators around the world to revise the safe limits of these toxins to ensure the health of consumers. Therefore, the concentrations of HMs in vegetables and soil and their risk to humans are of great public concern [25].

2.1.2. Sources of heavy metal contamination

The likely sources of the trace metal in the river are due to rural, urban, industrial and agricultural runoff in the river basins, although there could be a contribution from natural and point sources. They are introduced naturally through geographical phenomena such as volcanic eruptions, weathering of rocks; leaching into rivers, lakes and oceans due to the action of wind as well as a variety of human activities (anthropogenic sources) such as mining, smelting, electroplating, burning of fossil fuels such as coal, gasoline and kerosene oil and other industrial processes such as the discharge of agricultural, industrial and domestic waste, contain metal residues in their waste streams [26].

The paint industry in our country has sewage that contains washing solvents, suspended solids and some dangerous chemicals such as heavy metals that need to be treated before disposal. However, this amount of liquid waste discharged is dangerous for the nearby river if left untreated [9]. The presence of pollutants such as heavy metals in urban and industrial wastewater leads to contamination of water and soil. Household wastewater, wastewater, commercial wastewater, atmospheric deposition and traffic-related emissions that are transported into the sewage system carry a number of pollutants and enrich municipal wastewater with heavy metals [27].

Most of the heavy metals in water are commonly associated with industrial discharges. These metals are therefore dangerous as they tend to bioaccumulate in the food chain and are harmful to humans and animals. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time compared to the chemical concentration in the environment. The

risk to human and animal health from heavy metals is increased by their long-term persistence in the environment [28]. In addition, the prolonged accumulation of heavy metals in food can lead to chronic effects in the kidneys and liver of humans and cause a disruption of numerous biochemical processes that lead to cardiovascular, nervous, kidney and bone diseases [29].

2.2. Cadmium

2.2.1. Occurrence

Cadmium is comparatively rare in the environment with an average frequency similar to that of the transition metals of the second and third series (e.g. silver and mercury). It is widespread in the earth's crust at an average concentration of around 0.1 mg/kg. The highest concentrations of cadmium compounds in the environment are accumulated in sedimentary rocks, and marine phosphates contain around 15 mg/kg of Cd [30]. At elevated levels of cadmium, it is typically found in association with sulphide ores of zinc and sometimes with ores of copper and lead. The primary mineral compounds of cadmium are with otavite ($CdCO_3$), greenockite (CdS), sphalerite (ZnS), smithonite ($ZnCO_3$) [31].

2.2.2. Sources of cadmium

Cadmium is often a by-product of the extraction of lead, zinc and copper from their respective ores such as carbonaceous shale, coal and other fossil fuels are also sources of cadmium. Volcanism is the largest natural source of cadmium [32]. The largest sources of cadmium contamination of ground and surface water are sewage sludge, metal works in mines (process water), battery recycling plants and waste from electroplating plants. Anthropogenic sources of cadmium in the soil and in the groundwater are the use of commercially available fertilizers and the disposal of sewage sludge as a soil improver [33].

2.2.3. Effects of cadmium

Human exposure to Cd includes eating contaminated food, smoking cigarettes, and working in cadmium-contaminated workplaces and in the primary metal industry. The effects of cadmium toxicity in humans include kidney damage, mutagenic and carcinogenic effects. Cadmium

adversely affects several important enzymes. It can cause painful bone disease, red blood cell destruction, and kidney damage [34]. Chronic toxicity of Cd in children includes damage to the respiratory tract, kidneys, skeleton, and cardiovascular system, as well as the development of lung, kidney, prostate, and gastric cancers [35]. Low chronic exposure to cadmium can have adverse health effects, including gastrointestinal, hematological, musculoskeletal, renal, neurological and reproductive effects. The main target organ for cadmium after chronic oral exposure is the kidney, as cadmium tends to accumulate in the kidneys. The International Agency for Research on Cancer (IARC) has classified Cd and its compounds as potential carcinogens for humans. This classification is based on data on lung cancer in humans from occupational inhalation [36].

2.3. Lead

2.3.1. Occurrence

Natural lead accumulation occurs around hydrothermal deposits and base metal ores, most frequently as the mineral galena (PbS), but also as oxidation products of lead sulfide ores such as angelsite ($PbSO_4$) and cerussite ($PbCO_3$). Lead is distributed in low concentrations in sedimentary rocks and soils. Lead is a common metallic contaminant in hazardous waste landfills, especially in battery shredding and recycling plants. In fact, lead is the most commonly recycled metal: around 50% of lead production is secondary lead. About 70% of the world's lead goes to lead-acid batteries [37].

2.3.2. Sources of lead

Lead is one of the oldest metals known to mankind and is released into surface water through paints, solders, pipes, building materials, gasoline, etc. the continued use of leaded gasoline in many developing countries. It is seldom found in its elemental form; however, it is part of several ores, including its own (galena, PbS). Pb has many industrial and commercial uses. Pb sources in the environment include car exhaust, industrial waste water, sewage sludge and pesticides [38]. Atmospheric precipitation is usually the main source of lead in freshwater. Due to its high toxicity, the use of lead in some products has been discontinued. Lead is no longer

used in home paints due to concerns about the toxic effects of accidental ingestion of paint splinters or inhalation of misted lead from decaying paint [39].

2.3.3. Effects of lead

It is poisonous in very low concentrations in water and is known to cause brain damage in mammals. Exposure to Pb can occur through inhalation of contaminated dust particles and aerosols or through ingestion of contaminated food and water. Lead poisoning in humans damages the kidneys, liver, heart, brain, skeleton and nervous system [40]. The first symptoms of poisoning associated with lead exposure may include headache, fatigue, memory loss, and irritability. Lead poisoning can lead to disorders of hemoglobin synthesis and anemia. Lead can also be transmitted through breast milk. Anemia, colic, impaired vitamin D metabolism and growth retardation result from lead exposure in infants and toddlers. In children, chronic exposure to low levels of lead can reduce their capacity for intelligence. According to the International Agency for Research on Cancer (IARC), lead is a possible carcinogenic substance in humans [29].

2.4. Chromium

2.4.1. Occurrence

Chromium is a Group VI transition metal, the name of which refers to the variety of colors associated with its various oxidation states. Chromite is the only ore of chromium metal. It consists mainly of chromium and iron oxides (Cr_2O_3 68%), the most important ore is chromite ($FeCr_2O_4$). It can also occur as lead chromate ($PbCrO_4$). Only two of these oxidation states are known in nature. In minerals that crystallized in the earth's interior, chromium occurs exclusively in Cr^{+3} oxidation state and the second largest contributor to groundwater, soil and sediment contamination [41].

2.4.2. Sources of chromium

The release of chromium compounds into the environment occurs mainly through the electroplating, leather tanning, metal finishing, corrosion protection and pigment manufacturing

industries [42]. The paint manufacturing industry is the primary source of toxic chromium metal release into the surrounding aquatic environment. Chromium is often released into the environment through wastewater and fertilizers [43]. Chromium has two stable forms, namely the trivalent Cr (III) and the hexavalent Cr (VI) form, later one is more toxic. In addition, high concentrations of chromium are mutagenic, and carcinogenic. Chromium also has a detrimental effect on physiological processes in plants such as photosynthesis and mineral nutrition [44].

2.4.3. Effects of chromium

A medical warning was issued that inhalation of dust containing chromium in the high oxidation states (IV) and (VI) was associated with malignant growth in the airways and painless perforation of the nasal septum under trivalent and hexavalent states, the most stable and most common the earth are surroundings. Hexavalent chromium is considered to be the greatest threat due to its high solubility, ability to penetrate cell membranes, and strong oxidizing ability. The health effects associated with Cr (VI) exposure include occupational asthma, eye irritation and damage, perforated eardrum, irritation of the respiratory tract, kidney damage, liver damage, pulmonary congestion and edema, upper abdominal pain, nasal irritation and damage, respiratory cancer, skin irritation and erosion and Discoloration of teeth. Some workers may also develop an allergic skin reaction called allergic contact dermatitis [45].

Hexavalent chromium compounds including chromates of Ca, Zn, and Pb are readily soluble in water, poisonous and carcinogenic. In addition, chromium compounds have been linked to slow-healing ulcers. It has also been reported that chromate compounds can destroy DNA in cells [46].

2.5. Nickel

2.5.1. Occurrence

Nickel is a transition element with atomic number 28 and an atomic weight of 58.69. Oxide or silicate ores such as garnierite, $(NiMg)_6Si_4O_{10}(OH)_8$, nickel sulfides consist of NiS_2, $Ni(OH)_2$, $NiCO_3$ or $NiNO_3$. Other nickel oxides such as nickel oxide Ni_2O_3 and nickel peroxide NiO_2 are unstable in alkaline solutions and decompose with the release of oxygen. In acidic regions, however, these solids dissolve with the formation of Ni^{2+} [47].

2.5.2. Sources of nickel

Sources of nickel in wastewater are marine cruise wastewater, industrial applications and the chemical industry. Due to anthropogenic or geo-genic sources, industrial activities and natural environmental conditions have led to the entry of nickel into the soil and water from nickel mining and electroplating [48].

2.5.3. Effects of nickel

Human exposure to Ni is through food, air and water. Previous studies have shown that uptake of nickel-contaminated dust was the main exposure path to the heavy metal by local residents compared to inhalation and dermal paths [49]. When exposed to nickel, a person may have elevated levels of Ni in their tissues and urine. The adverse effects of nickel on human health can include dermatitis, allergies, organ disease, and respiratory cancer, and nickel compounds are known to be carcinogenic in both human and animal models [50

2.6. Determination of metals using flame atomic absorption spectroscopy

Atomic absorption spectrometry (AAS) is a widely used method for determining trace and ultra-trace elements in all types of samples. With AAS, a light beam passes the sample. Depending on the concentration of the element, a certain proportion of the light is absorbed. By comparing the intensity of the original beam and the beam after passing the sample, the concentration of the element can be calculated. Since each element absorbs light of a defined wavelength, the AAS instruments have individual light sources for each element. Typically, AAS is a method of determining only a single element per analysis.

The advantage is that this analytical method enables the determination of elements in very low mass concentrations (g L^{-1} range). Depending on the expected mass concentration range and the amount of sample available, the analysis can be performed with either flame AAS (FAAS) or graphite tube AAS (GF-AAS). For the former, a sample volume of a few mL is required, for the latter, only small amounts of sample are required. Therefore, GF-AAS allows much lower detection limits than FAAS. GF-AAS can also be used to enrich the analyte by repeatedly pipetting the sample into the graphite tube.

By changing the pipetting speed of the auto sampler, the effects of physical disturbances due to the higher viscosity of solutions such as saliva or sweat solutions can be minimized. Chemical modifiers can be used to avoid chemical inference. AAS is a single element method that operates in a sequential mode. It is suitable for monitoring studies of a specific element such as Cd, Cr, Ni and Pb, which even in very low mass concentrations have negative effects on human health. The disadvantage of GF-AAS is the long analysis time per sample and much care is required, on a much more limited scale, typically for low trace elements. An important application of this method is the monitoring of wastewater [51]. The block diagram of FAAS and GF-AAS is shown in Figure 1. In general, hollow cathode lamps are used as source, flame or graphite furnace as atomizer and grating as wavelength selector and photomultiplier as detector.

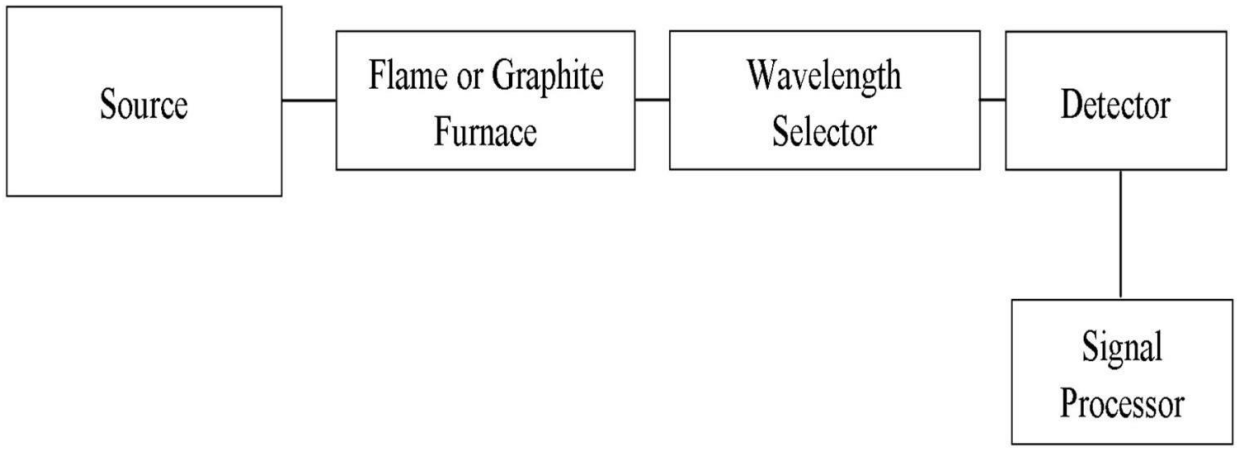

Figure 1**:** Schematic diagram for FAAS and GFAAS

Comparing FAAS and GFAAS to quantify a few elements also examines some of these practical concerns, while experimental pollution monitoring requires the determination of trace levels of toxic heavy metals. The flame atomic absorption spectrometry technique, which offers fast multi-elemental analysis, low running costs, very good precision, suffers from poor sensitivity in the determination of heavy metals in environmental samples such as natural water and other real samples, is used for high levels of screening and is used for uses a limited range of common elements [52].

The disadvantage is the high detection limit and the matrix interference, which can be overcome by combining a suitable enrichment technique with subsequent AAS determination. Enrichment methods that can be used for water samples include solvent extraction, precipitation, resin chelation, and various chromatographic techniques. These enrichment methods offer low detection limits and also help to avoid matrix interference when analyzing real samples [53]. Beer law states that the absorption is directly proportional to the concentration of the analyte [54]. FAAS uses two types of flame: 1, air/acetylene flame, 2, nitrous oxide/acetylene flame. The type of flame depends on the thermal stability of the analyte. The acetylene flame formed in the air is around 2300°C, while the acetylene-nitrous oxide flame is around 30°C [55]. In general, cadmium, chromium, lead and nickel can be determined with an air/acetylene flame [56].

2.6.1. Beer’s Law

Many compounds absorb ultraviolet (UV) or visible (Vis) light. A beam of monochromatic radiation of radiation power Po, directed onto a sample solution. Absorption takes place and the radiation beam leaving the sample has radiation power. The amount of radiation absorbed can be measured in several ways: Experimental measurements are usually made in terms of transmission (T), which is defined as follows: T = I/Io where I is the light intensity after passing through the sample and Io is the initial one Light intensity. The relationship between A and T is: A = - log T = log (I/Io). Modern absorption instruments can usually display the data as transmittance, percentage transmittance, or absorption. An unknown concentration of an analyte can be determined by measuring the amount of light a sample absorbs and applying Beer's law.

If the absorption coefficient is not known, the unknown concentration can be determined using a standard-derived absorbance versus concentration working curve. Beer's Lambert law is an equation that relates absorption to concentration, path length, and molar absorptivity. The molar absorption capacity depends on the substance, the solvent and lambda. The units for the molar absorption capacity are L/Mol.cm for the concentration in mol/L. Mathematically, the Lambert-Beer law can be expressed as A = cl. This equation can be used to determine an unknown concentration or estimate the absorbance of a particular solution as long as three of the values in the equation are known. The Beer Law shows that absorption is directly related to concentration. To determine the molar absorption capacity, the slope of the best-fit straight line is divided by the path length (usually l). It should be noted that there are conditions in which deviations from the Beer Law occur. This happens if the concentrations are too high or because of the sensitivity of the instruments [57].

2.7. Sample preparation methods

2.7.1. Dry Ashing Method

Dry ashing procedures are sample preparations that have been described by several authors. Usually the samples are pre-dried at a temperature of 105°C and then dry-ashed in a muffle furnace at temperatures between 500°C and 600°C until white ash is obtained. The residue is then diluted with a mineral acid and the element content of this solution is measured [58].

2.7.2. Wet Digestion

During wet digestion, organic material is destroyed through the use of heat and acids. A weighed sample is placed in a decomposition vessel, treated with acid and heated for several hours. The samples are digested with HNO_3, HNO_3 and $HClO_4$ or HNO_3 and H_2SO_4 [59]. Depending on the technique and the heating vessel used, heating plates or decomposition blocks are used to maintain a temperature of 80°C to 125°C. After the digestion, the sample is cooled, diluted to a certain volume and analyzed directly. The digestion method depends on the elements considered, the method of determination and the volatility of the elements.

The main advantage of wet digestion is that the elemental loss due to volatilization is eliminated because the digestion takes place at a low temperature. The main disadvantage of a wet digestion process is that it is subject to reagent contamination and requires operator attention. For this reason, wet ash is preferred to dry ash in this process [60]. Nitric acid is preferred over sulfuric acid because the probability of the formation of insoluble salts, as might be the case with H_2SO_4, is lower [61].

3. EXPERIMENTAL

3.1. Description of the study

This study was carried out in the city of Addis Ababa. The selection of these sampling points was based on the consideration of the relative amount of wastewater that discharges pollutants into the surrounding area and the accessibility of the investigation points. Primary data was obtained from the four selected locations, Kadisco Paint, Zemilli Paint, Nefas Silk Paint, Abay paint industries. The wastewater sampling was carried out using random sampling methods. The extracted wastewater sample was analyzed for the presence and amount of heavy metal concentration in the laboratory of Chemistry at the Faculty of Science at Addis Ababa University.

3.1.1. Chemicals and reagent

All reagents used for the waste water analysis were analytically pure. Deionized water was used for all preparation and dilution purposes throughout the study. Nitric acid (69% HNO_3, LR, Breckland Scientific Supplies, UK) and detergent and dilute nitric acid have been used for general washing of plastic and glassware.

3.1.2. Apparatus

Devices used: -Heating plate, eye glasses, gloves, filter paper, conical 125 mL flasks (Erlenmeyer) as well as 150 mL beakers and 250 mL volumetric flasks. The pipettes and burette were thoroughly rinsed with dilute nitric acid solution and double-distilled water before their final use.

3.1.3. Sample collection

The paint wastewater samples were taken at random within four days from four different paint industries in Addis Ababa. Three representative samples were selected for each paint industry. Devices for collecting wastewater samples for metal analysis have been made from plastic. Wastewater samples were collected at the discharge point and outside the discharge point with 2 L polyethylene bottles, which were cleaned thoroughly with hydrochloric acid, then washed twice with distilled water, rinsed again with the waste water sample to be collected and then stored in the transparent polyethylene bottles and in a cooler place. Care was taken not to introduce errors during sampling and storage due to contamination from improperly cleaned sampling devices and sample containers [54].

3.1.4. Sample transportation and storage

Paint wastewater samples were filtered using Whatman No.41 (0.45 m pore size) filter paper prior to preservation to remove foreign materials. Filter papers are acid washed and dried before use. After filtering the sample, the filtrate was taken as a sample for the dissolved metal content and acidified for preservation purposes [62]. The sample was preserved by adding 1.5 mL of concentrated HNO_3 per liter of sample, as stated in environmental sampling and analysis for

metals, in order to prevent the deposition of heavy metals on the container wall and stored at low temperature until use. The samples were stored on an inert temperature for the wastewater and were transported to the laboratory for analysis. The sampling devices were cleaned before sampling and at the end of sampling. Deionized water is used for rinsing [63].

3.1.5. Procedure

100 ml of the four filtered samples were placed in a 250 mL Erlenmeyer flask, then 10 mL concentrated nitric acid (69%, HNO_3) was added to each flask and placed on a hot plate at a temperature of 90°C for one hour to 10 mL remains. The beaker was then removed from the stove and the sides washed with deionized water. Each of the digested wastewater samples was diluted with deionized water in a 100 mL volumetric flask to make up for the loss of water through evaporation. A blank digest was also carried out in the same way. The blank solution contained all reagents except wastewater. All samples were triple digested. The digestions were analyzed for the toxic heavy metals using FAAS in the analytical chemistry laboratory of the University of Addis Ababa [56]

3.1.6. Instrumental calibration

Calibration curves were created to determine the heavy metal concentration in the sample solutions. Intermediate standard solution 10 mg/L of each metal was prepared from sock standard solutions containing 1000 mg/L cadmium, chromium, lead and nickel. Four series of working standard solutions were used for the determination of Cd, Cr, Pb and Ni in paint waste water. Appropriate working standards were prepared for each metal solution by diluting the intermediate solution with deionized water using the standard stocks containing 1000 mg/L of each element in 1.5 mL of concentrated nitric acid solution. The working standards were then successively sucked into the flame atomic absorption spectrometer and their absorbance recorded in Table (9). Calibration curves were plotted at different points for each metal standard solution using absorbance versus concentration (mg/L).

3.1.7. Detection limit of method

The detection limit of method is defined as the minimum measurable concentration of the analyte. In other words, it is the lowest analyte concentration that can be distinguished from statistical fluctuations in a blank value, which normally correspond to the signal of the blank value three times the standard deviation of the blank value. Three blank samples were prepared for the determination of each cadmium, chromium, lead and nickel by FAAS. The SD of the three replicate blanks was calculated to determine the detection limit of the method. The detection limit of the method (MDL) was then calculated according to the equation LOD = 3SD/m. Where, SD = standard deviation of the blank, m = slope of the calibration curve [64].

3.1.8. Recovery test

Recovery is one of the most common techniques used to validate analytical results and to assess the extent to which the method is acceptable for its intended purpose. In this study, the validity of the digestion process, the precision and accuracy of FAAS was ensured by adding a standard of known concentration to the water sample. The spiked and unspiked water samples were digested according to the method used for digesting the waste water sample. Then the percentage recoveries of the analytes were calculated [65]. Percentage recovery = (spiked sample /Unspined sample) x100% analyte added. The acceptable ranges of the percentage recovery for the heavy metal analysis were within 80-120% [66].

3.1.9. Heavy metal analysis

Immediately after calibration with the standard solutions, the sample solutions were sucked into the FAAS device and the metal concentrations were read off directly [67]. The concentrations of Cd, Cr, Pb and Ni in the extracted water were estimated with FAAS. The device ZEEnit700P # 150Z7P1025 Tech: Flame equipped with air/acetylene flame, with a hollow cathode lamp was used to analyze the analyte metals Cd, Cr, Pb and Ni in paint waste water samples. A reagent blank was analyzed and stripped from the samples to correct for reagent contamination and other environmental sources of error. The samples were analyzed in triplicates and the blank value determinations in triplicates were carried out in the same way during the analysis.

4. RESULTS AND DISCUSSION

4.1. Data interpretation

Percentage recoveries and method validation

The results of the percentage recoveries (Table 5) for the metals examined in the wastewater samples of the four paint industries were 93% for Cr, 95% for Cd, 96% for Pb and 97.98% for Ni, which is within the acceptable range of 80-120% [66]. This confirms that the digestion methods used in this study have been validated by the spiking method and it is evident that the results obtained with FAAS were accurate and suggest that the samples were well prepared, efficiently and without contamination handled for the Analysis used FAAS instrument was precise.

The values of the correlation coefficient (R^2) closer to the absolute value of (1) indicate that there is a strong relationship between the variables to be determined, while values closer to zero (0) indicate that there is no linear relationship between absorbance and concentration [68]. As can be seen in Figures 2, 3, 4 and 5, the correlation coefficient of the metals was 0.998 for Cd, 0.999 for Cr, 0.999 for Pb and 0.999 for Ni, respectively, suggesting a strong relationship between the variables were examined because the values of R^2 were closer to one and therefore the performance of the FAAS instrument could provide accurate results. The correlation coefficient of the element was determined by plotting prepared standards against their corresponding absorbance.

Limit of detection

The standard deviation of the three replicate blanks was calculated to determine the limit of detection of the method. The limit of detection (LOD) was then calculated according to the equation LOD = 3SD/m. The detection limit of the method was calculated from (Table 6) 0.0014 for Cd, 0.0007 for Cr, 0.0014 for Pb and 0.0001 for Ni. As can be seen in (Table 6), the method detection limit for Cd, Cr and Pb was found to be below the instrumental detection limit. This may indicate that there are no problems with the procedure or the analytical equipment.

Level of heavy metals in wastewater samples

The distribution of heavy metals (Cr, Cd, Pb and Ni) in effluent samples from the four paint industries was examined. Color wastewater samples were taken from the drain and taken to the laboratory for chemical analysis. The results obtained showed that the concentration of heavy metals was in the order of Cd> Ni> Cr> Pb as shown in (Table 4). In addition, the concentration of the four metals was above the permitted limit values of the WHO (2006) and EPA (2003), which could lead to negative effects on human health and the environment.

Table 1: Instrumental operating conditions for the determination of Cr, Cd, Pb and Ni in wastewater samples from the paint industry were used by using FAAS

Elements	Wave length λ in (nm)	Slit width in (nm)	Current in (mA)	Energy in (EV)	PMT [V]	Slope
Cd	228.8	1.2	2	69.2	312	0.046
Cr	357.9	0.2	4	72	420	0.009
Pb	283.3	1.2	2	74.6	460	0.002
Ni	232.0	0.2	3	71.4	342	0.005

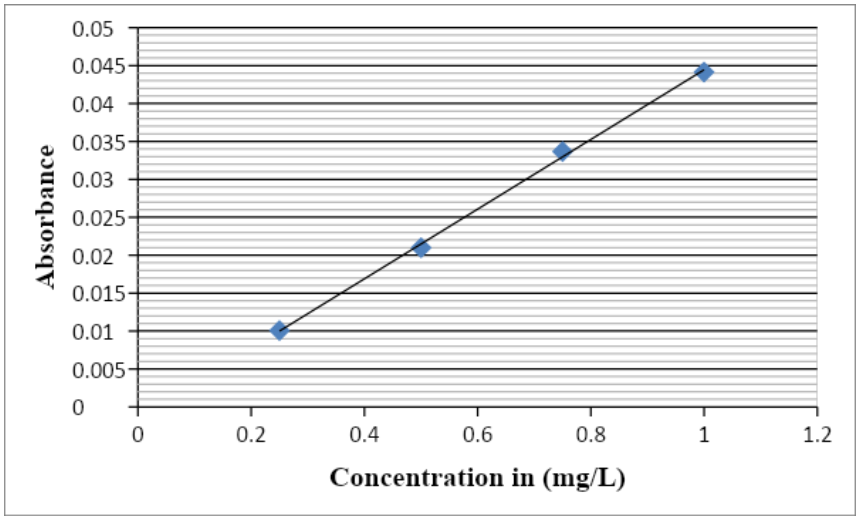

Figure 2: Calibration curve of Cd standard solution

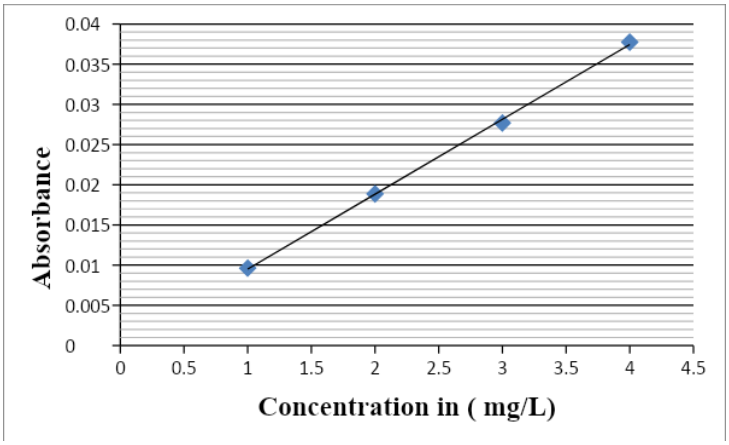

Figure 3: Calibration curve of Cr standard solution

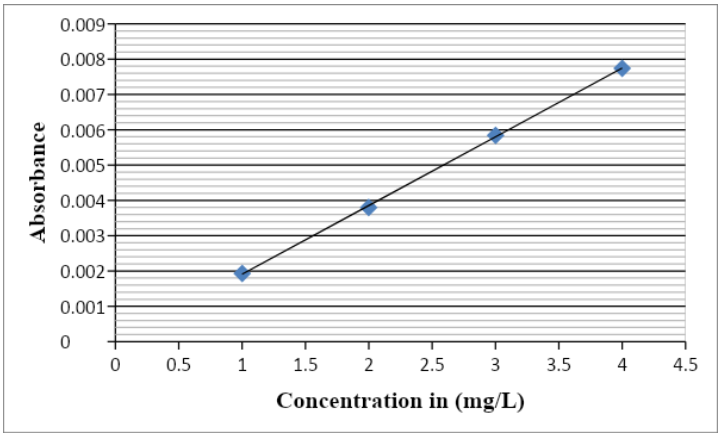

Figure 4: Calibration curve of Pb standard solution

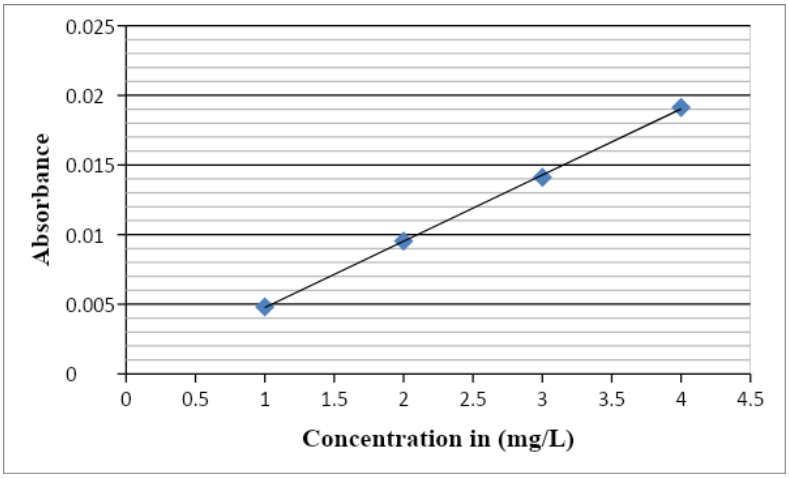

Figure 5: Calibration curve of Ni standard solution

Table 2: The concentrations Cr, Cd, Pb and Ni the four paint industries effluents

Industries	Cd (mg/L)	Pb (mg/L)	Cr) (mg/L)	Ni (mg/L)
Kadisco paint	1.0281	0.8109	1.781	4.188
Zemilli paint	1.8426	0.7441	1.67	3.5586
Nefas silk paint	5.6025	0.6884	0.5438	2.725
Abay paint	3.1153	0.7492	1.5976	4.261

Table 3: Selected heavy metals in wastewater, as recommended by the WHO (2006) [69]

Heavy metals	Concentration (mg/L)
Cadmium	0.003
Chromium	0.10
Lead	0.05
Nickel	0.02

Table 4: Concentrations of heavy metals in paint waste water and their comparison with the maximum permissible limits of the ES EPA (2003) [70].

Heavy metals	Concentration (ppm)
Cadmium	0.01
Chromium	0.05
Lead	0.05
Nickel	0.10

Table 5: Percentage recovery, unspiked, added and spiked solution

Element	Unspiked	Added	Spiked	% Recovery
Cd	1.0291	0.2056	1.2247	95%
Cr	1.7798	0.3559	2.1107	93%
Ni	4.201	0.8402	5.0243	97.9%
Pb	0.8135	0.1627	0.9697	96%

Table 6: Regression equation, correlation coefficient, and LOD

Heavy metal	Regression equation	R^2	LOD (mg/L)
Cd	Y=0.046x-0.0015	0.9987	0.0014
Cr	Y=0.0093x+0.0002	0.9993	0.0007
Pb	Y=0.0019x-4E-05	0.9997	0.0014
Ni	Y=0.0048x+1E-05	0.9997	0.0001

Table 7: Blank solutions prepared in the laboratory

Heavy metals	mean value of each blank (mg/L)
Cadmium	0.029
Chromium	0.0115
Lead	0.080
Nickel	0.0019

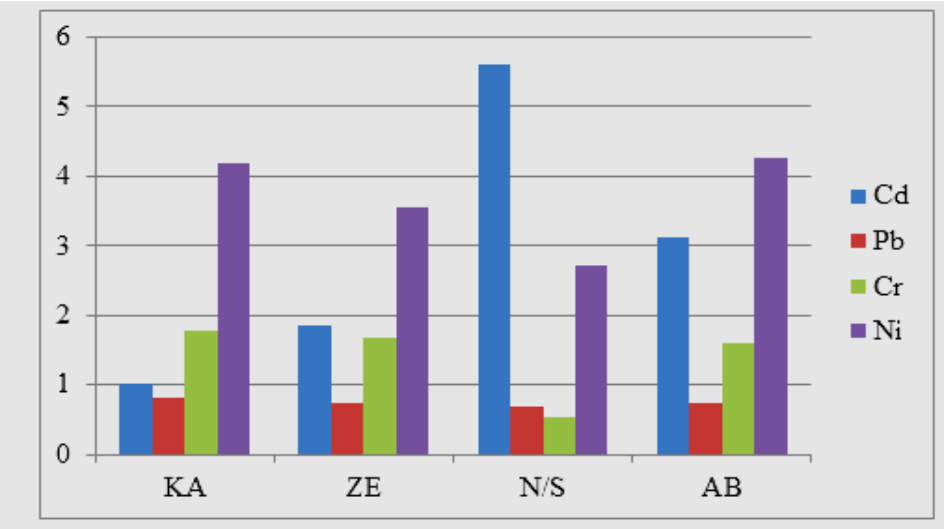

Figure 6: Heavy metal content in wastewater from four different paint industries in Addis Ababa, Ethiopia.

According to the result shown in (Table 3), Cd was detected in all wastewater samples from the paint factories. However, Cd is mainly found in the Nefas silk paint factory which recorded 5.6025 mg/L among all other paint factories and a minimum of 1.028 mg/L in the Kadisco paint factory. All values are above the permissible limit value of the ES, which is 0.01 mg/L (Table 2), and the safe limit values recommended by the WHO for Cd in wastewater, which is 0.003 mg/L (Table 4). Cd contamination can pose a risk to the receiving environment.

The experimental data showed that the mean Cr concentration in wastewater samples was detected at all locations (Table 3), which is much higher than the permissible limit values of 0.05 mg/L and 0.05 mg/L according to ES (Table 2) and WHO (Table 4). The experimental data show that the average chromium content in wastewater samples was least 0.5438 mg/L for wastewater samples from the Nefas silk paint industry and a maximum of 1.781 mg/L for wastewater samples from the Kadisco paint industry (Figure 5). The result shows that the paint

manufacturing industry is the main source of toxic chromium metal being released into the surrounding aquatic environment.

In the present study it was found that the maximum concentration (0.8109 mg/L) of Pb in the wastewater samples from the Kadisco paint factory and the minimum concentration of 0.6884 mg/L in the wastewater samples from Nefassilk paint industry were found (Table 3). Here, too, the lead concentration detected in all paint manufacturing industries is much higher than the permissible limit value of 0.05 mg/L set by the EPA (2003) and the safe limit values recommended by the WHO for Pb in wastewater from paint factories are 0.01 mg/L (Table 2).

The maximum mean concentration of Ni (4.261 mg/L) was found in wastewater from the Abay paint industry and a minimum of 2.725 mg/L in wastewater samples from the Nefas Silk paint factory (Table 3). The results of the present study show that the Ni concentration in various industrial wastewaters is above the permissible limit value of EPA (Table 2) of 0.10 mg/L and the safe limit values recommended by the WHO for Ni in wastewater of 0.02 was mg/L (Table 4).

5. CONCLUSIONS

Industrial effluent is widely used for irrigation in the city of Addis Ababa. Industrial wastewater contains toxic heavy metals that can be ingested by crops and vegetables. The presence of large amounts of the heavy metals Pb, Ni, Cr and Cd in wastewater from the paint industry indicates that the area is contaminated by these toxic metals and is unsuitable for human, animal health and vegetable production. Based on the data from the present study, it is very important to note that the concentrations of toxic heavy metals for wastewater in various areas of the four wastewater discharges of the paint industry are above the maximum recommended limits of the ESEPA and the WHO. In particular, the Kadisco and Abay paint industry has released a large amount of toxic heavy metals, in addition to this Nefas silk paint industry has released a large amount of a toxic cadmium metal, so the authority needs to review this paint industry. The environmental protection agency and health department must inform farmers not to use this contaminated wastewater for irrigation purposes for growing vegetables and crops. The government concerned must verify whether or not the paint industry is using wastewater treatment technologies and take appropriate corrective measures or penalties to protect people's health from these toxic heavy metals. Industrial owners must use inexpensive wastewater treatment technology to minimize the release of these toxic heavy metals directly into the environment and the river without treatment. The EPA, the Health Department and the Agriculture Department should raise awareness of the toxicity effects of these heavy metals on human health to farmers.

6. RECOMMENDATIONS

Therefore, it is recommended that the consumption of vegetables grown on the industrially contaminated agricultural land around the wastewater area become a high risk to human health and animals, unless corrective action is taken in existing pollution laws to prevent both to stop growing vegetables and to raise community awareness of the risks associated with industrially contaminated farmland.

All concerned bodies such as the Environmental Protection Agency, the Health Department, the Department of Agriculture, the Addis Ababa Water and Wastewater Department, universities and research organizations are working together to create a common platform to reduce the risks associated with industrially contaminated wastewater and to move towards it focus on an appropriate strategy for industrial waste management and integrated into industrial development.

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APPENDIX:

Table 8: The concentrations of Cd, Cr, Ni and Pb from four paint industry effluents samples

Cd

Sample	Conc. (mg/L)
NS a	5.612
NS b	5.5931
NS c	5.6132
KAD a	1.025
KAD b	1.032
KAD c	1.027
AB a	3.1271
AB b	3.1096
AB c	3.1092
Z a	1.8370
Z b	1.8409
Z c	1.8501

Cr

Sample	Conc. (mg/L)
NS a	0.5396
NS b	0.5391
NS c	0.5527
KAD a	1.780
KAD b	1.762
KAD c	1.801
AB a	1.591
AB b	1.593
AB c	1.609
Z a	1.657
Z b	1.687
Z c	1.666

Ni

Sample	Conc. (mg/L)
NS a	2.710
NS b	2.739
NS c	2.726
KAD a	4.166
KAD b	4.197
KAD c	4.201
AB a	4.285
AB b	4.240
AB	4.259
Z a	3.534
Z b	3.570
Z c	3.572

Pb

Sample	Conc. (mg/L)
NS a	0.6775
NS b	0.6834
NS c	0.7045
KAD a	0.8119
KAD b	0.8068
KAD c	0.8141
AB a	0.7445
AB b	0.7486
Z a	0.7588
Z b	0.7308
Z c	0.7427

Where:-NS = Nefas silk, KA = Kadisco paint, AB = Abay paint, ZN = Zemilli paint

Table 9:-Working standard concentrations of Cd, Cr, Pb and Ni.

Cd

Standard	Concentration	Absorbance
1	0.25	0.01007
2	0.5	0.021
3	075	0.03369
4	1	0.04415

Cr

Standard	Concentration	Absorbance
1	1	0.00963
2	2	0.01887
3	3	0.02768
4	4	0.03774

Pb

Standard	Concentration	Absorbance
1	1	0.00193
2	2	0.0038
3	3	0.00584
4	4	0.00774

Ni

Standard	Concentration	Absorbance
1	1	0.00481
2	2	0.00954
3	3	0.01412
4	4	0.01913

Figure 7: Picture of wastewater samples